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**(54) ELECTROLYTE
COMPOSITION,
ELECTROCHEMICAL CELL,
PHOTOELECTROCHEMICAL
CELL, AND NONAQUEOUS
SECONDARY CELL
BATTERY**

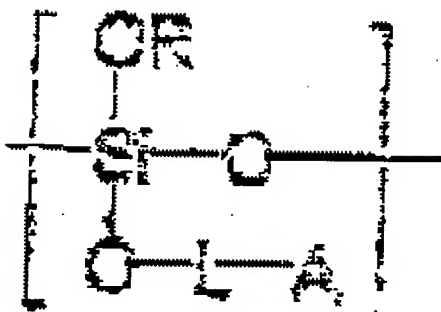
(57) Abstract:

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Title: JP2002343440A2: ELECTROLYTE COMPOSITION, ELECTROCHEMICAL CELL, PHOTOELECTROCHEMICAL CELL, AND NONAQUEOUS SECONDARY CELL BATTERY

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Inventor: YASUDA TAKAYASU;
WARIISHI KOJI;

Assignee: FUJI PHOTO FILM CO LTD
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(72)Inventor : YASUDA TAKAYASU
WARIISHI KOJI

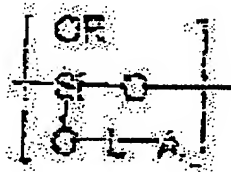
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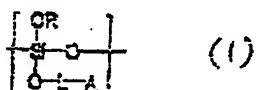
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(54) 【発明の名称】 電解質組成物、電気化学電池、光電気化学電池、非水二次電池

(57) 【要約】 (修正有)

【課題】 耐久性、イオン導電率に優れた電解質組成物、さらに当該電解質組成物を用いた、耐久性、電気特性（光電変換特性）に優れた電気化学電池、非水二次電池、及び光電気化学電池を提供する。

【解決手段】 一般式（1）で示されるポリシロキサン構造を繰り返し単位として有する液晶化合物を含有する電解質組成物、それを用いた電気化学電池、光電気化学電池及び非水二次電池である。



【一般式（1）中、Rはアルキル基、Lは単結合又は2価の連結基を、Aは液晶性置換基を表す。但し、液晶性置換基はイオン性の基を有してもよく、その場合、液晶性置換基はその対イオンを含む。】

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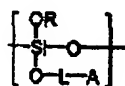
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【特許請求の範囲】

【請求項1】 下記一般式(1)で示されるポリシロキサン構造を繰り返し単位として有する液晶化合物を含有する電解質組成物。

【化1】



一般式(1)

【一般式(1)中、Rはアルキル基を表し、Lは単結合又は2価の連結基を表す。Aは液晶性置換基を表す。但し、液晶性置換基はイオン性の基を有してもよく、その場合、液晶性置換基はその対イオンを含む。】

【請求項2】 前記液晶性置換基が、メソゲン基を含むアニオン部位と、その対カチオンからなるカチオン部位とで構成される塩であることを特徴とする請求項1記載の電解質組成物。

【請求項3】 前記対カチオンが、アルカリ金属イオンであることを特徴とする請求項2に記載の電解質組成物。

【請求項4】 前記液晶性置換基が、メソゲン基を含むカチオン部位と、その対アニオンからなるアニオン部位とで構成される塩であることを特徴とする請求項1記載の電解質組成物。

【請求項5】 前記対アニオンが、ヨウ素アニオンと、スルホンアミド、ジスルホンイミド、N-アシルスルホンアミド、カルボン酸、スルホン酸、アルコール、活性メチレン、及び活性メチレンの解離したアニオンとからなる群から選択されることを特徴とする請求項4に記載の電解質組成物。

【請求項6】 前記液晶化合物が、重合することにより得られる高分子液晶化合物であることを特徴とする請求項1～5記載の電解質組成物。

【請求項7】 請求項1～6のいずれかに記載の電解質組成物を含むことを特徴とする電気化学電池。

【請求項8】 導電性支持体上に、請求項1～6のいずれかに記載の電解質組成物を含む電荷送達層、色素で増感された半導体を含む感光層、及び対極を有することを特徴とする光電気化学電池。

【請求項9】 請求項1～6のいずれかに記載の電解質組成物を含むことを特徴とする非水二次電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、液晶化合物を含む電解質組成物、さらに電解質組成物を用いた電気化学電池、特に非水二次電池および光電気化学電池に関する。

【0002】

【従来の技術】 非水二次電池や色素増感太陽電池などの電気化学電池に用いられる電解質とは、目的に応じたキ

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ャリアイオンを含み、そのイオンを電極間に輸送する機能(イオン伝導という)を持つ媒体である。例えば、非水二次電池の代表であるリチウム二次電池では、リチウムイオンの輸送が、色素増感太陽電池では、ヨウ素イオンおよびヨウ素三量体イオンの伝導性が電気化学電池の性能に大きな影響を及ぼす。これら電池においては、一般に、イオン伝導性が高い溶媒系が電解質として多用されているが、電池に組み込んだ際の溶媒の枯渇や漏れが電池の耐久性を低下させるなどの問題があった。また、リチウム二次電池においては溶液を密閉するため、金属容器を用いなければならないため、電池質量が重くなり、電池形状にも自由度を持たせることが困難であった。このような溶液系電解質の欠点を克服するため、近年、種々の電解質が提案されている。溶液電解質をポリマーマトリックスに浸潤させたいわゆるゲル電解質(特公昭61-23945号広報、特公昭61-23947号広報)は、溶液系電解質に対するイオン伝導度の低下が小さく電池性能を落とさないが、溶媒の揮発を完全に抑止することはできていない。また、塩をポリエチレンオキシドなどのポリマーに溶解したポリマー電解質

(K. Murata, Electrochimica Acta, Vol. 40, No. 13-14, p2177-2184, 1995年)は、溶液系電解質の問題を解決するものとして期待されるが、イオン伝導度は未だ十分ではない。一方、対アニオンが BF_4^- 、 $(CF_3SO_2)_2N^-$ などのイミダゾリウム塩やピリジニウム塩は、室温で液状の室温溶融塩であり、リチウムイオン電池用の電解質として、提案されているが、電解質の機械的強度とイオン伝導性とは相反し、溶融塩自身の粘性を上げたり、ポリマーを含有させるなどの手段で、機械的強度を強くした場合にはイオン伝導度の低下が見られる。さらに、上記のような電解質では、イオン伝導性の温度依存性が大きく、特に低温でのイオン伝導性が不十分であった。

【0003】ところで、光エネルギーを電気エネルギーに変換する太陽光発電は単結晶シリコン太陽電池、多結晶シリコン太陽電池、アモルファスシリコン太陽電池、テルル化カドミウムやセレン化インジウム銅等の化合物太陽電池が実用化、もしくは研究開発の対象となっているが、普及させる上で製造コスト、原材料の確保、エネルギーペイバックタイムの長さなどの課題点を克服する必要がある。一方、大面積化や低価格化を指向した有機材料を用いた太陽電池もこれまでに多く提案されているが、変換効率が低く、耐久性も悪いという問題があった。

【0004】こうした状況の中で、Nature(第353巻、第737～740頁、1991年)および米国特許4927721号等に、色素によって増感された酸化物半導体を用いた光電変換素子(以後、色素増感光電変換素子と略す)およびこれを用いた光電気化学電池の

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技術が開示された。この電池は負極として機能する光電変換素子、電荷移動層および対極からなる。光電変換素子は導電性支持体および感光層からなり、感光層は表面に色素が吸着した半導体を含む。電荷移動層は酸化還元体からなり、負極と対極（正極）との間で電荷輸送を担う。上記特許で提案された光電気化学電池では、電荷移動層としてヨウ化カリウム等の塩を電解質とする水溶液（電解液）が用いられた。この方式は安価で、比較的高いエネルギー変換効率（光電変換効率）が得られる点で有望であるが、長期にわたって使用すると電解液の蒸散、枯渇により光電変換効率が著しく低下したり、電池として機能しなくなることが問題であった。

【0005】この問題に対し、電解液の枯渇防止方法として、WO95/18456号に低融点化合物であるイミダゾリウム塩を電解質とする方法が記載されている。この方法によれば、従来、電解質の溶媒として用いていた水や有機溶剤が不要、あるいは少量で済むため、耐久性の改善は見られたが、未だ耐久性は不十分であり、またイミダゾリウム塩を高濃度にするると粘度が高くなるとともに電荷輸送能が低下し、光電変換効率が低くなるという問題があった。さらには、トリアゾリウム塩を電解質とする方法もあるが、この方法においてもイミダゾリウム塩と同様の問題が生じる。

【0006】上記のように、リチウムイオン二次電池や太陽電池などの電気化学電池の電解質として機械的強度とイオン伝導性を両立することは、非常に困難な課題である。

【0007】これらを解決する一つの方法として、液晶性化合物を電解質組成物に含有させることが提案されている。これらの例として、アルキレンオキシ基などイオンに対する配位能を持つ部位とメソゲン基を有する化合物（特開平11-86629号）、ポリエチレンオキシド分子鎖中にメソゲン基が導入された化合物（特開平4-323260号）、ポリエチレンオキシドの側鎖に液晶性部位を有する化合物（特開平11-116792号）、ポリシロキサン樹脂の側鎖にオリゴオキシエチレンスパーサーを介してメソゲン基が導入された化合物（特公平6-19923号）などが示されている。これらは、カチオンと錯形成することにより電解質塩を溶解しイオンを伝導する運動性の高い柔軟な部位と、機械的強度を保つために分子集合させるための剛直部位（メソゲン基）から構成されている。

【0008】ところで、重原らの最近の研究（Journal of Power Source, 92巻, 120-123頁, 2001年）から、電解質が電気化学電池の中で効率良く機能するためには、イオン伝導度が高いことと他に、キャリアイオンがより選択的に伝導すること、すなわちキャリアイオン輸率の高いことが性能上重要であることがわかってきている。例えば、リチウムイオン電池においては、リチウムイオン輸率が高いこ

と、ヨウ素アニオンがキャリアとなる色素増感太陽電池においてはヨウ素アニオン輸率の高いことが望ましい。前述した液晶性化合物においては、ポリアルキレンオキシドなどのカチオンと相互作用の強い基がカチオンを束縛し、カチオン輸率の低下を招いている。また、カチオンとの錯形成により、分子運動性が低下するためイオン伝導度そのものの向上も期待できない。

【0009】一方、上述に示しような特公平6-19923号により開示されているポリシロキサンの側鎖にメソゲン基を導入した電解質組成物には、アルキル置換されたポリシロキサンが例示されており、この電解質組成物は、カチオンを強く束縛するオリゴオキシエチレン部位がイオン伝導の媒体となっており、高いカチオン輸率は期待できない現状である。

【0010】

【発明が解決しようとする課題】本発明は、前記従来における諸問題を解決し、以下の目的を達成することを課題とする。即ち、本発明の第一の目的は、耐久性、イオン伝導率に優れた電解質組成物を提供することである。さらに本発明の第二の目的は、当該電解質組成物を用いた、耐久性、電気特性（光電変換特性）に優れた電気化学電池、非水二次電池、及び光電気化学電池を提供することである。

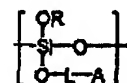
【0011】

【課題を解決するための手段】上記課題は、以下の手段により解決される。即ち、本発明は、

<1>下記一般式（1）で示されるポリシロキサン構造を繰り返し単位として有する液晶化合物を含有する電解質組成物。

【0012】

【化2】



一般式（1）

【0013】【一般式（1）中、Rはアルキル基を表し、Lは単結合又は2価の連結基を表す。Aは液晶性置換基を表す。但し、液晶性置換基はイオン性の基を有してもよく、その場合、液晶性置換基はその対イオンを含む。】

【0014】<2>前記一般式（1）におけるAが表す液晶性置換基が、メソゲン基を含むアニオン部位と、その対カチオンからなるカチオン部位とで構成される塩であることを特徴とする前記<1>に記載の電解質組成物。

<3>前記対カチオンが、アルカリ金属イオンであることを特徴とする前記<2>に記載の電解質組成物。

<4>前記一般式（1）におけるAが表す液晶性置換基が、メソゲン基を含むカチオン部位と、その対アニオンからなるアニオン部位とで構成される塩であることを特徴とする前記<1>に記載の電解質組成物。

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<5>前記対アニオンが、ヨウ素アニオンと、スルホンアミド、ジスルホンイミド、N-アシルスルホンアミド、カルボン酸、スルホン酸、アルコール、活性メチレン、及び活性メチンの解離したアニオンとからなる群から選択されることを特徴とする前記<4>に記載の電解質組成物。

<6>前記液晶化合物が、重合することにより得られる高分子液晶化合物であることを特徴とする前記<1>～<5>記載の電解質組成物。

[0015] <7>前記<1>～<6>のいずれかに記載の電解質組成物を含むことを特徴とする電気化学電池。

<8>導電性支持体上に、前記<1>～<6>のいずれかに記載の電解質組成物を含む電荷輸送層、色素で増感された半導体を含む感光層、及び対極を有することを特徴とする光電気化学電池。

<9>前記<1>～<6>のいずれかに記載の電解質組成物を含むことを特徴とする非水二次電池。

[0016]

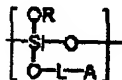
[発明の実施の形態] 以下、本発明を詳細に説明する。本発明の電解質組成物は、下記一般式(1)で示されるポリシロキサン構造を繰り返し単位として有する液晶化合物を含有してなる。

[0017] この特定の液晶化合物は、下記一般式

(1)で示されるように、アルコキシ置換されたポリシロキサン構造を繰り返し単位として有する。このアルコキシ置換されたポリシロキサン構造は、運動性が高く、かつ、カチオンを強く束縛せずに電解質塩を溶解できるため、オキシエチレン基よりも高いカチオン輸率とイオン伝導性が実現できる。このように、アルコキシ置換されたポリシロキサン構造は、その主鎖により電解質塩を溶解しイオンを伝導する媒体となり、一方で、その側鎖の剛直な部位(液晶性置換基)は液晶性によって分子集合してイオン伝導媒体とはミクロに相分離した構造支持体を形成し、イオン伝導媒体の運動性を低下させることなく、電解質組成物のマクロな機械的強度をもたらす。このため、特定の液晶化合物を含有する本発明の電解質組成物は、耐久性と電荷輸送性能に優れる。

[0018]

[化3]



一般式(1)

[0019] 一般式(1)中、Rはアルキル基(好ましくは炭素原子数(以下C数)が1～24であり、より好ましくは(C数)が1～10であり、直鎖状であっても分岐鎖状であってもよく、例えばメチル、エチル、プロピル、ブチル、i-プロピル、i-ブチル、ペンチル、ヘキシル、オクチル、2-エチルヘキシル、1-オクチル、デシル、ドデシル、テトラデシル、2-ヘキシルデシル、ヘキサデシル、オクタデシル、シクロヘキシルメチル、オクチルシクロヘキシル]を表す。さらにRは、置換基を有していてもよく、好ましい置換基としては、置換していてもよいアルキル基(好ましくは炭素原子数(以下C数)が1～24であり、より好ましくは(C数)が1～10であり、直鎖状であっても分岐鎖状であってもよく、例えばメチル、エチル、プロピル、i-プロピル、i-ブチル、ペンチル、ヘキシル、オクチル、2-エチルヘキシル、1-オクチル、デシル、ドデシル、テトラデシル、2-ヘキシルデシル、ヘキサデシル、オクタデシル、シクロヘキシルメチル、オクチルシクロヘキシル]、置換していても縮環していてもよいアリール基(好ましくはC数6～24、例えばフェニル、4-メチルフェニル、3-シアノフェニル、2-クロロフェニル、2-ナフチル)、置換していても縮環していてもよい複素環基(含窒素複素環基のときは環中の窒素が4級化していてもよい。好ましくはC数2～24、例えば4-ピリジル、2-ピリジル、1-オクチルピリジニウム-4-イル、2-ピリミジル、2-イミダゾリル、2-チアゾリル)、アルコキシ基(好ましくはC数1～24、例えばメトキシ、エトキシ、ブトキシ、オクチルオキシ、メトキシエトキシ、メトキシペンタ(エチルオキシ)、アクリロイルオキシエトキシ、ペンタフルオロプロポキシ)、アシルオキシ基(好ましくはC数1～24、例えばアセチルオキシ、ベンゾイルオキシ)、アルコキシカルボニル基(好ましくはC数2～24、例えばメトキシカルボニル、エトキシカルボニル)、シアノ基、フルオロ基、アルコキシカルボニル基、シアノ基、および重合性基(好ましくはビニル基、アクリロイル基、メタクリロイル基、スチリル基、桂皮酸残基など)が挙げられる。

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ル、デシル、ドデシル、テトラデシル、2-ヘキシルデシル、ヘキサデシル、オクタデシル、シクロヘキシルメチル、オクチルシクロヘキシル]を表す。さらにRは、置換基を有していてもよく、好ましい置換基としては、置換していてもよいアルキル基(好ましくは炭素原子数(以下C数)が1～24であり、より好ましくは(C数)が1～10であり、直鎖状であっても分岐鎖状であってもよく、例えばメチル、エチル、プロピル、ブチル、i-プロピル、i-ブチル、ペンチル、ヘキシル、オクチル、2-エチルヘキシル、1-オクチル、デシル、ドデシル、テトラデシル、2-ヘキシルデシル、ヘキサデシル、オクタデシル、シクロヘキシルメチル、オクチルシクロヘキシル]、置換していても縮環していてもよいアリール基(好ましくはC数6～24、例えばフェニル、4-メチルフェニル、3-シアノフェニル、2-クロロフェニル、2-ナフチル)、置換していても縮環していてもよい複素環基(含窒素複素環基のときは環中の窒素が4級化していてもよい。好ましくはC数2～24、例えば4-ピリジル、2-ピリジル、1-オクチルピリジニウム-4-イル、2-ピリミジル、2-イミダゾリル、2-チアゾリル)、アルコキシ基(好ましくはC数1～24、例えばメトキシ、エトキシ、ブトキシ、オクチルオキシ、メトキシエトキシ、メトキシペンタ(エチルオキシ)、アクリロイルオキシエトキシ、ペンタフルオロプロポキシ)、アシルオキシ基(好ましくはC数1～24、例えばアセチルオキシ、ベンゾイルオキシ)、アルコキシカルボニル基(好ましくはC数2～24、例えばメトキシカルボニル、エトキシカルボニル)、シアノ基、フルオロ基、アルコキシカルボニル基、シアノ基、および重合性基(好ましくはビニル基、アクリロイル基、メタクリロイル基、スチリル基、桂皮酸残基など)が挙げられる。

[0020] 一般式(1)中、Lは単結合または2価の連結基を表す。2価の連結基の例としては、 $-(CH_2)_n-$ (ここでnは1～15の整数を示す)、 $-CH_2CH_2(OCH_2CH_2)_n-$ (ここでnは1～10の整数を示す)、 $-CH=CH-$ 、 $-CH=N-$ 、 $-N=N-$ 、 $-N(O)=N-$ 、 $-COO-$ 、 $-COS-$ 、 $CONH-$ 、 $-COCH_2-$ 、 $-CH_2NH-$ 、 $-CO-$ 、 $-CH=CH-COO-$ 、 $-CH=CH-CO-$ 、 $-(C\equiv C)-$ (ここでnは1～3の整数を示す)やこれらの組合せなどが好ましく、 $-(CH_2)_n-$ (ここでnは3～10の整数を示す)、 $-CH_2CH_2(OCH_2CH_2)_n-$ (ここでnは2～8の整数を示す)やこれらの組合せがさらに好ましい。

[0021] 一般式(1)中、Aは液晶性置換基を表すが、液晶性置換基としては、メンゲン基が挙げられ、例えば"Flussige Kristalle in Tabellen II", Dietrich Demus and Horst Zischke, 7-18

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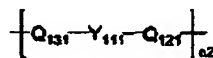
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(1984). 記載されているものが挙げられる。中でも、下記一般式(11)で表されるものが好ましい。

【0022】

【化4】



一般式(II)

【0023】一般式(11)中、 Y_{111} は、2価の4ないし7員環置換基またはそれらから構成される縮合環置換基を表す。 Q_{111} および Q_{121} は、それぞれ2価の連結基または単結合を表し、 $n2$ は1、2または3を表し、 $n2$ が2または3の時、複数の Y_{111} 、 Q_{111} および Q_{121} は、それぞれ同じであっても、異なってもよい。

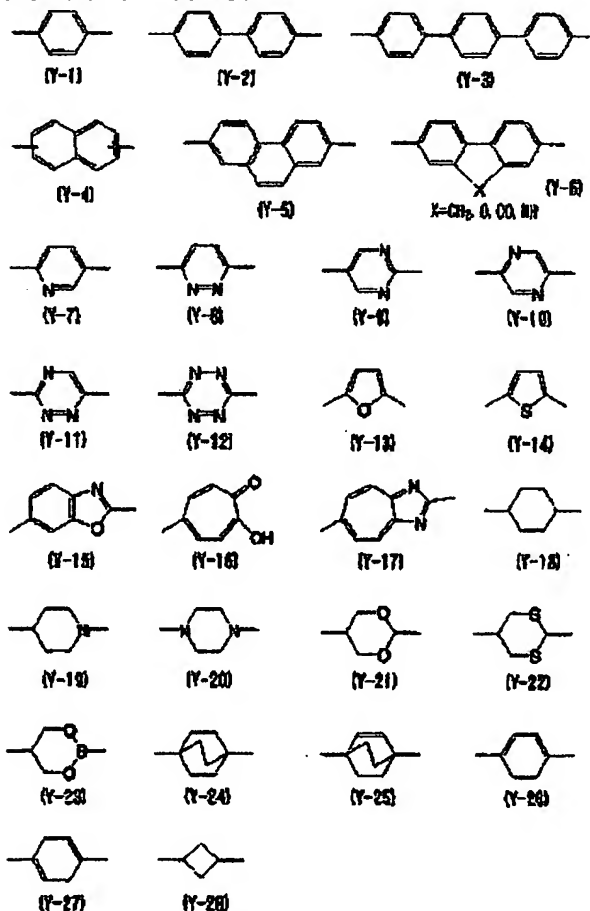
【0024】一般式(11)中、 Q_{111} および Q_{121} は、それぞれ2価の連結基または単結合を表す。2価の連結基の例としては、 $-\text{CH}=\text{CH}-$ 、 $-\text{CH}=\text{N}-$ 、 $-\text{N}=\text{N}-$ 、 $-\text{N}(\text{O})=\text{N}-$ 、 $-\text{COO}-$ 、 $-\text{COS}-$ 、 $-\text{CONH}-$ 、 $-\text{COCH}_2-$ 、 $-\text{CH}_2\text{CH}_2-$ 、 $-\text{OCH}_2-$ 、 $-\text{CH}_2\text{NH}-$ 、 $-\text{CH}_2-$ 、 $-\text{CO}-$ 、 $-\text{O}-$ 、 $-\text{S}-$ 、 $-\text{NH}-$ 、 $-(\text{CH}_2)_{n1}-$ 、 $-\text{CH}=\text{C}$ 20
H-COO-、 $-\text{CH}=\text{CH}-\text{CO}-$ 、 $-(\text{C}\equiv\text{C})$ *

*、 $_{n1}$ やこれらの組合せなどが好ましく、 $-\text{CH}_2-$ 、 $-\text{CO}-$ 、 $-\text{O}-$ 、 $-\text{CH}=\text{CH}-$ 、 $-\text{CH}=\text{N}-$ 、 $-\text{N}=\text{N}-$ やこれらの組合せがさらに好ましい。また、これらにおいて水素原子が置換されたものであってもよい。 Q_{111} および Q_{121} は、単結合であることが特に好ましい。

【0025】一般式(11)中、 Y_{111} は、2価の4、5、6または7員環置換基、またはそれらから構成される縮合環置換基を表し、6員環芳香族基、4ないし6員環の飽和または不飽和脂肪族基、5または6員環複素環基、またはそれらの縮合環であることがさらに好ましく、これらの例として、下記式(Y-1)~(Y-27)の置換基が挙げられるが、これらに限定されない。また、これらの組合せであってもよい。これらの置換基の中でさらに好ましいものは、(Y-1)、(Y-2)、(Y-18)、(Y-19)、(Y-21)、(Y-22)であり、特に好ましいものは、(Y-1)、(Y-2)、(Y-21)である。

【0026】

【化5】



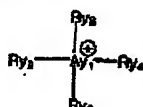
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【0027】液晶性置換基は、イオン性の基を有してもよく、その場合、液晶性置換基はその対イオンを含み、所謂、アニオン部位とカチオン部位とで構成される塩構造を形成してなる。この液晶置換基が塩構造を有することで、特定の液晶化合物は、電解質を調整する際、イオン性である液晶化合物の対イオンをキャリアイオンとすることができる。このため、別途、キャリアイオンを塩の形で添加する必要がなく、キャリアイオン以外の可動性イオンが含まれないため、キャリアイオンの純率を高めることができる。この場合、液晶性置換基として液晶性を付与する基、例えばメソゲン基はアニオン部位とカチオン部位の少なくとも一方に含まれる。液晶性を付与する基を含まない、或いは一般式(Ⅰ)におけるしと直接連結していない方のアニオン部位、又はカチオン部位は有機イオン(有機アニオン、有機カチオン)でも、無機イオン(無機アニオン、無機カチオン)でもよい。

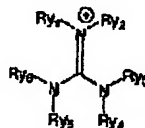
【0028】液晶性置換基の好適な具体的構成として *



式(Ⅲ-a)



式(Ⅲ-b)



式(Ⅲ-c)

【0031】一般式(Ⅲ-a)のQ₁は、窒素原子と共に、5または6員環の芳香族カチオンを形成しうる原子団を表し、R₁は、置換もしくは無置換のアルキル基、重台性基、または置換もしくは無置換のアルケニル基を表す。

【0032】一般式(Ⅲ-b)のA₁は、窒素原子またはリン原子を表し、R₁、R₂、R₃およびR₄は、各々独立に、置換もしくは無置換のアルキル基、重台性基、または置換もしくは無置換のアルケニル基を表す。ただし、R₁、R₂、R₃およびR₄の3つ以上が同時にアリール基であることはない。また、R₁、R₂、R₃およびR₄の内2つ以上が互いに連結してA₁を含む非芳香族環を形成してもよい。

【0033】一般式(Ⅲ-c)のR₁、R₂、R₃、R₄、R₅およびR₆は、各々独立に、置換もしくは無置換のアルキル基、重台性基、または置換もしくは無置換のアルケニル基を表し、それらの内、2つ以上が互いに連結して環構造を形成してもよい。

【0034】一般式(Ⅲ-a)、(Ⅲ-b)、および(Ⅲ-c)で表されるカチオンは、Q₁またはR₁～R₆を介して多量体を形成してもよい。

【0035】一般式(Ⅲ-a)中、窒素とともに芳香族5または6員環のカチオンを形成しうる原子団Q₁の構成原子は、好ましくは炭素、酸素、窒素、酸素および硫黄より選択される。

【0036】Q₁で完成される6員環として、好ましくはピリジン、ピリミジン、ピリダジン、ピラジン、トリ

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*は、メソゲン基を含むアニオン部位と、その対カチオンからなるカチオン部位とで構成される塩、或いはメソゲン基を含むカチオン部位と、その対アニオンからなるアニオン部位とで構成される塩が挙げられる。これらアニオン部位及びカチオン部位のいずれか一方が一般式

(Ⅰ)におけるしと連結されてなる。

【0029】カチオン部位にメソゲン基を含む場合、そのカチオン部位(正電荷を持つ置換基)として好ましい構造は、一般式(Ⅲ-a)、(Ⅲ-b)又は(Ⅲ-c)で表される構造である。この時、メソゲン基は、一般式(Ⅲ-a)～(Ⅲ-c)におけるR₁～R₆、またはQ₁の置換基として含まれることが好ましい。また、前記一般式(Ⅰ)で示される繰り返し単位からなる原子団R₁～R₆、またはQ₁の置換基として含まれることが好ましい。

【0030】

【化6】

アジンであり、より好ましくはピリジンである。

【0037】Q₁で完成される芳香族5員環として、好ましくは、オキサゾール、チアゾール、イミダゾール、ピラゾール、イソオキサゾール、チアジアゾール、オキサジアゾール、トリアゾールであり、より好ましくはオキサゾール、チアゾール、イミダゾールである。特にオキサゾール、イミダゾールが好ましい。

【0038】一般式(Ⅲ-a)、(Ⅲ-b)および(Ⅲ-c)中のR₁～R₆は、各々独立に、置換もしくは無置換のアルキル基(好ましくは炭素原子数(以下C数)が1～24であり、直鎖状であっても分岐鎖状であってもよく、また環状であってもよく、例えばメチル、エチル、プロピル、ブチル、1-プロピル、ペンチル、ヘキシル、オクチル、2-エチルヘキシル、1-オクチル、デシル、ドデシル、テトラデシル、2-ヘキシルデシル、オクタデシル、シクロヘキシル、シクロペンチル)、重台性基(好ましくはビニル基、アクリロイル基、メタクリロイル基、スチリル基、桂皮酸残基など)、または置換もしくは無置換のアルケニル基(好ましくはC数が2～24であり、直鎖状であっても分岐鎖状であってもよく、例えばビニル、アリル)を表し、好ましくはC数3～18のアルキル基またはC数2～18のアルケニル基を表し、より好ましくはC数4～6のアルキル基を表す。

【0039】一般式(Ⅲ-a)、(Ⅲ-b)および(Ⅲ-c)中のQ₁およびR₁～R₆は置換基を有していてもよく、好ましい置換基の例としては、ハロゲン

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原子(F, Cl, Br, I)、シアノ基、アルコキシ基(メトキシ、エトキシ、ブトキシ、オクチルオキシ、メトキシエトキシ、メトキシベンタ(エチルオキシ)、アクリロイルオキシエトキシ、ペンタフルオロプロポキシなど)、アリーロキシ基(フェノキシなど)、アルキルチオ基(メチルチオ、エチルチオなど)、アシル基(アセチル、プロピオニル、ベンゾイルなど)、スルホニル基(メタンスルホニル、ベンゼンスルホニルなど)、アシルオキシ基(アセトキシ、ベンゾイルオキシなど)、スルホニルオキシ基(メタンスルホニルオキシ、トルエン
10 スルホニルオキシなど)、ホスホニル基(ジエチルホスホニルなど)、アミド基(アセチルアミノ、ベンゾイルアミドなど)、カルバモイル基(N, N-ジメチルカルバモイル、N-フェニルカルバモイルなど)、アルキル基(メチル、エチル、プロピル、イソプロピル、シクロプロピル、ブチル、2-カルボキシエチル、ベンジルなど)、アリール基(フェニル、トルイルなど)、複素環基(例えば、ピリジル、イミダゾリル、フラニルなど)、アルケニル基(ビニル、1-プロペニルなど)、アルコキシ基アシルオキシ基(アセチルオキシ、ベン
20 イルオキシなど)、アルコキシカルボニル基(メトキシカルボニル、エトキシカルボニルなど)、および重合性基(好ましくはビニル基、アクリロイル基、メタクリロイル基、スチリル基、桂皮酸残基など)が挙げられる。

【0040】カチオン部位にメソゲン基を含む場合、その対アニオンとして好ましくは、無機アニオンとしてハロゲンアニオン(Cl^- , Br^- , I^-)、ヨウ素三量体アニオン(I_3^-)、 NCS^- 、 BF_4^- 、 PF_6^- 、 O_3C^- 、 Ph_3B^- 、 AsF_6^- 、 SbF_6^- 、及び $\text{B}_{10}\text{C}_{11}$
30 O_{11}^- と、有機アニオンとしてスルホンアミド、ジスルホンイミド、N-アシルスルホンアミド、カルボン酸、スルホン酸、アルコール、活性メチレン、及び活性メチンの解離したアニオンとからなる群から選択されることが好ましい。より好ましくは、ヨウ素アニオン(I^- , I_3^-)と、有機アニオンとしてスルホンアミド、ジスルホンイミド、N-アシルスルホンアミド、カルボン酸、スルホン酸、アルコール、活性メチレン、及び活性メチ
40 ンの解離したアニオンとからなる群から選択される。さらに好ましくはヨウ素アニオン(I^- , I_3^-)と、有機アニオンとしてスルホン酸、ジスルホンイミド、及びN-アシルスルホンアミドの解離したアニオン(例えば(C_6F_5) $_3\text{SO}_3^-$ 、(C_6F_5) $_3\text{SO}_3^-$) N^- で表わされるイミドアニオン(n, mはそれぞれ6以下の正の整数)、 C_6F_5 $_3\text{SO}_3^-$ で表わされるフルオロスルホン酸アニオン(nは6以下の正の整数)等)とからなる群から選択される。特に好ましくは、ヨウ素アニオン(I^- , I_3^-)である。このヨウ素アニオンは、特定の

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液晶化合物を、ヨウ素イオンがキャリアとなる太陽電池用電解質用途として用いる場合に有利である。

【0041】アニオン部位にメソゲン基を含む場合、そのアニオン部位(負電荷を持つ置換基)として好ましいものは、スルホンアミド、ジスルホンイミド、N-アシルスルホンアミド、カルボン酸、スルホン酸、アルコール、活性メチレン、および活性メチンのプロトン解離したアニオンである。

【0042】アニオン部位にメソゲン基を含む場合、その対カチオンとして好ましくは、有機カチオンとして前述の一般式(III-a)、(III-b)および(III-c)で表される構造のカチオン、無機カチオンとしてはリチウムイオンが好適に挙げられる。これらの中でも特にリチウムイオンが好適である。このリチウムイオンは、特定の液晶化合物をリチウムイオン電池やリチウム電池用電解質として用いる場合に有利である。

【0043】液晶性置換基(イオン性の基を有する場合、その対イオンも含む)には、末端基、またはメソゲン基とイオン性を示す有機イオンとを連結する基として、アルキル基またはアルケニル基を含むことが好ましい。これらのアルキル基またはアルケニル基の炭素数は6から25が好ましく、6から18が更に好ましい。また、置換基を有していてもよく、好ましい置換基としては、一般式(I)のRにおける置換基として前述したものが挙げられる。

【0044】液晶性置換基として、特に好ましい構成は、本発明の電解質組成物をリチウムイオン電池やリチウム電池用途に用いる場合、一般式(I)におけるLと連結される部位がメソゲン基を含むアニオン部位であり、そのカチオン部位となる対イオンがリチウムイオンである構成である。一方、ヨウ素イオンがキャリアとなる太陽電池用途に用いる場合、一般式(I)におけるLと連結される部位がメソゲン基を含むカチオン部位であり、そのアニオン部位となる対アニオンがヨウ素イオンである構成であることが好ましい。

【0045】液晶性置換基として、アニオン部位の共役酸のpKaは1以下であることが、電解質においてキャリアとなるイオン(例えば、リチウムイオンやヨウ素イオンなど)の解離度を高める観点から好ましく、7以下であることがさらに好ましい。

【0046】以下、一般式(I)で示されるポリシロキサン構造の具体例P-1~P-28を示すが、本発明はこれら具体例に限定されるわけではない。なお、この具体例で示される構造を繰り返し単位として有する液晶化合物を、例示化合物P-1~P-28とする。

【0047】

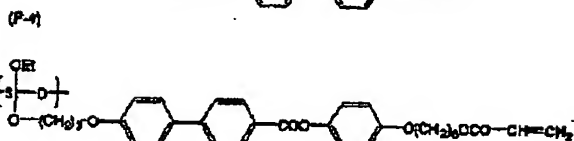
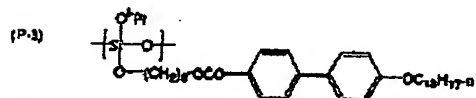
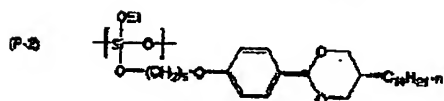
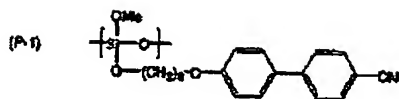
【化7】

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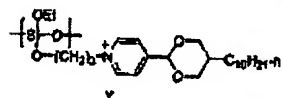
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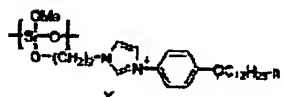


[0048]

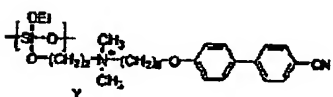
* * [化8]



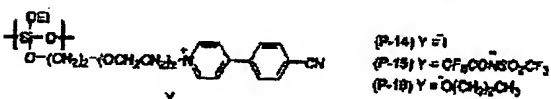
(P-5) Y = I⁻
 (P-6) Y = N(SO₂CF₃)₂⁻
 (P-7) Y = CF₃COO⁻



(P-8) Y = I⁻
 (P-9) Y = N(SO₂CF₃)₂⁻
 (P-10) Y = BF₄⁻



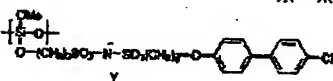
(P-11) Y = I⁻
 (P-12) Y = H₃COOC-C(=O)-(SO₂CF₃)₂⁻
 (P-13) Y = BF₄⁻



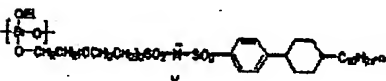
(P-14) Y = I⁻
 (P-15) Y = CF₃COOCH₂CH₂SO₂CF₃⁻
 (P-16) Y = O(CH₂)₆CH₃

[0049]

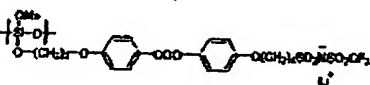
* * [化9]



(P-17) Y = I⁻
 (P-18) Y = H₃C-N(CH₂)₂-N(CH₂)₂-CH₂CH₃



(P-19) Y = I⁻
 (P-20) Y = H₃C-N(CH₂)₂-N(CH₂)₂-CH₂CH₃



(P-21)



(P-22)

[0050]

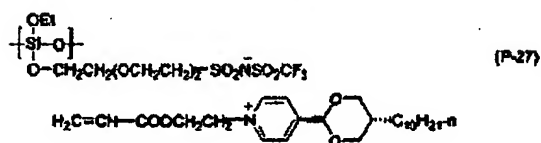
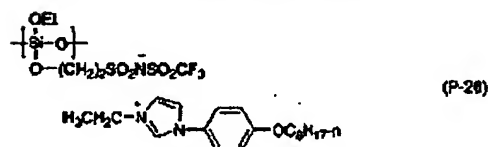
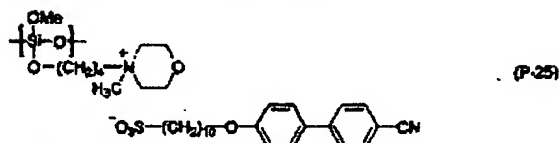
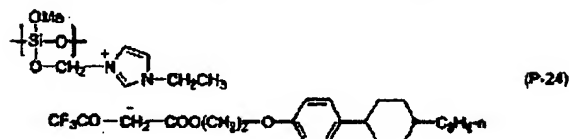
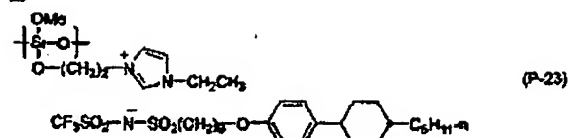
[化10]

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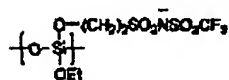
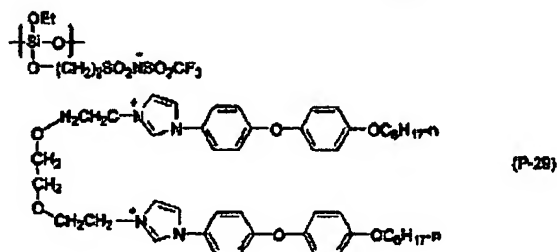
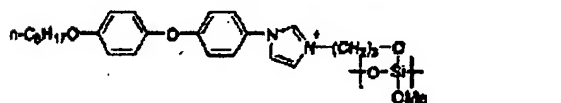
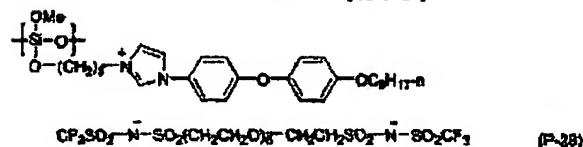
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[0051]

* * [化11]



[0052] 特定の液晶化合物は、重合性基を有し、それらを重合して得られる高分子化合物であってもよい。この高分子化合物の得る重合方法としては、大津隆行・木下雅悦共著：高分子合成の実験法（化学同人）や大津

隆行：講座重合反応論Ⅰラジカル重合（Ⅰ）（化学同人）に記載された一般的な高分子合成法であるラジカル重合法を用いることができる。熱重合開始剤を用いる熱重合法と光重合開始剤を用いる光重合法があり、好まし

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く使用される熱重合開始剤は、例えば、2, 2'-アゾビス(イソブチロニトリル)、2, 2'-アゾビス(2, 4-ジメチルバレロニトリル)、ジメチル2, 2'-アゾビス(2-メチルプロピオネート)などのアゾ系開始剤、ベンゾイルパーオキシドなどの過酸化物系開始剤等が含まれ、好ましく用いられる光重合開始剤の例には、 α -カルボニル化合物(米国特許2367661号、同2367670号の各明細書記載)、アンロインエーテル(米国特許244828号明細書記載)、 α -炭化水素置換芳香族アンロイン化合物(米国特許2722512号明細書記載)、多核キノン化合物(米国特許3046127号、同2951758号の各明細書記載)、トリアリールイミダゾールダイマーとp-アミノフェニルケトンとの組み合わせ(米国特許3549367号明細書記載)、アクリジンおよびフェナジン化合物(特開昭60-105667号公報、米国特許4239850号明細書記載)およびオキサジアゾール化合物(米国特許4212970号明細書記載)が含まれる。重合開始剤の好ましい添加量はモノマー(塩)総量に対し0.01質量%以上20質量%以下であり、さらに好ましくは0.1質量%以上10質量%以下である。重合により得られる高分子の好ましい分子量(数平均分子量)は、モノマー(塩)が単官能の場合は5,000~100万であり、さらに好ましくは1万~50万である。また、多官能モノマー(塩)の場合、あるいは架橋剤を用いた場合は、上記の分子量のポリマーが3次元網目構造を形成する。

【0053】本発明の電解質組成物を光電気化学電池の電解質に用いる場合、電荷キャリアとして、 I_2^- と I_3^- を含む電解質組成物を用いることが好ましく、それらは任意の塩の形で添加することができる。好ましいヨウ素塩の対カチオンとしては前述の一般式(III-a)、(II-b)または(III-c)で表されるものが挙げられる。 I_2^- 塩は、 I^- 塩存在下にヨウ素(I_2)を加え、電解質組成物中で生成させることが一般的である。その際、加えた I_2 と同量の I^- が生成する。

【0054】本発明の電解質組成物中の I^- の濃度は10~90質量%が好ましく、30~70質量%が更に好ましい。その際残りの成分が全て、特定の液晶化合物であることが好ましい。なお、この濃度は、前記特定の液晶化合物中の対イオンとして I^- が含まれる場合、これも含む濃度である。

【0055】 I_2^- は I^- の0.1~50モル%であることが好ましく、0.1~20モル%であることがより好ましく、0.5~10モル%であることがさらに好ましく、0.5~5モル%であることが最も好ましい。なお、この割合は、前記特定の液晶化合物中の対イオンとして I_2^- が含まれる場合、これも含む割合である。

【0056】本発明の電解質組成物にはさらに別の溶融塩を含んでもよく、好ましく用いられる溶融塩は、前記

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一般式(III-a)、(III-b)および(III-c)で示した有機カチオンと任意のアニオンとを組合せたものであり、アニオンとしては、ハロゲン化物イオン(Cl^- 、 Br^- 等)、 SCN^- 、 BF_4^- 、 PF_6^- 、 ClO_4^- 、 $(CF_3SO_2)_2N^-$ 、 $(CF_3CF_2SO_2)_2N^-$ 、 $CH_3SO_3^-$ 、 $CF_3SO_3^-$ 、 CF_3COO^- 、 Ph_3B^- 、 $(CF_3SO_2)_2C^-$ 等が好ましい例として挙げられ、 SCN^- 、 $CF_3SO_3^-$ 、 CF_3COO^- 、 $(CF_3SO_2)_2N^-$ および BF_4^- が更に好ましく挙げられる。また、特に、光電流向上の観点から、 LiI 、 CF_3COOLi 、 CF_3COONa 、 $LiSCN$ 、 $NaSCN$ などのアルカリ金属塩を含むことが好ましい。アルカリ金属塩の添加量は、0.02~2質量%程度であるのが好ましく、0.1~1質量%がさらに好ましい。

【0057】本発明の電解質組成物に、 LiI 、 NaI 、 KI 、 CsI 、 CaI_2 などの金属ヨウ化物、4級イミダゾリウム化合物のヨウ素塩、テトラアルキルアンモニウム化合物のヨウ素塩、 Br_2 と $LiBr$ 、 $NaBr$ 、 KBr 、 $CsBr$ 、 $CaBr_2$ などの金属臭化物、あるいは Br_2 とテトラアルキルアンモニウムブロマイド、ビリジニウムブロマイドなど4級アンモニウム化合物の臭素塩、フェロシアン酸塩-フェリシアン酸塩やフェロセン-フェリシニウムイオンなどの金属錯体、ポリ硫化ナトリウム、アルキルチオール-アルキルジスルフィドなどのイオウ化合物、ピオロゲン色素、ヒドロキノ-キノ-キノなどを含有させて用いることもできる。含有させる場合、これらの化合物の使用量は、電解質組成物全体の30質量%以下であることが好ましい。

【0058】本発明の電解質組成物では、前記特定の液晶化合物と併にとともに、好ましくは最大でこの化合物と同質量まで溶媒を使用することができる。

【0059】本発明の電解質組成物に使用する溶媒は、粘度が低くイオン移動度を向上したり、または誘電率が高く有効キャリア濃度を向上したりして、優れたイオン伝導性を発現できる化合物であることが望ましい。このような溶媒としては、エチレンカーボネート、プロピレンカーボネートなどのカーボネート化合物、3-メチル-2-オキサゾリジノンなどの複素環化合物、ジオキサン、ジエチルエーテルなどのエーテル化合物、エチレングリコールジアルキルエーテル、プロピレングリコールジアルキルエーテル、ポリエチレングリコールジアルキルエーテル、ポリプロピレングリコールジアルキルエーテルなどの鎖状エーテル類、メタノール、エタノール、エチレングリコールモノアルキルエーテル、プロピレングリコールモノアルキルエーテル、ポリエチレングリコールモノアルキルエーテルなどのアルコール類、エチレングリコール、プロピレングリコール、ポリエチレングリコール、ポリプロピレングリコール、グリセリンなどの多価アルコール類、アセトニトリル、グルタロジニ-

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リル、メトキシアセトニトリル、プロピオニトリル、ベンゾニトリルなどのニトリル化合物、カルボン酸エステル、リン酸エステル、ホスホン酸エステル等のエステル類、ジメチルスルフォキシド、スルフォランなど非プロトン性物質、水などを用いることができる。この中でも、エチレンカーボネート、プロピレンカーボネートなどのカーボネート化合物、3-メチル-2-オキサゾリジノンなどの複素環化合物、アセトニトリル、グルタロジニトリル、メトキシアセトニトリル、プロピオニトリル、ベンゾニトリルなどのニトリル化合物、エステル類が特に好ましい。これらは単独で用いても2種以上を併用してもよい。

【0060】溶媒としては、耐揮発性による耐久性向上の観点にて常圧（1気圧）における沸点は200℃以上が好ましく、250℃以上がより好ましく、270℃以上がさらに好ましい。

【0061】本発明の電解質組成物を、リチウムイオン電池などの電気化学電池に用いる場合には、電解質組成物中の化合物の少なくとも一種類は、リチウム元素（イオン）を含む化合物が好適に用いられるが、リチウム元素（イオン）の濃度としては、5重量%～100重量%が好ましく、20重量%から60重量%が更に好ましい。

【0062】本発明の電解質組成物は、化学反応および金属メッキ等の反応溶媒、CCD（電荷結合素子）カメラ、種々の電気化学電池（いわゆる電池）、電気化学センサー、光電気化学センサーなどに用いることができる。好ましくは非水二次電池（特に、リチウム二次電池）および後述する半導体を用いた光電気化学電池に用いられ、光電気化学電池に用いられることがより好ましい。

【0063】【電気化学電池】以下に、本発明の電解質組成物を利用した本発明の電気化学電池について説明する。本発明の電気化学電池は、前記本発明の電解質組成物を含有するので、優れた耐久性とイオン伝導性を示す。

【0064】本発明の電気化学電池は、電解質として、前記本発明の電解質組成物を含有する以外は、特に制限はなく、一般的な構成をとることができる。一般的な電気化学電池は、作用極と対極で電解質を挟んだ構成によりなり、作用極上で起こる酸化（還元）反応と対極で起こる還元（酸化）反応に対応して、電解質中のキャリアイオンが両極間を移動することにより機能する。後述する光電気化学電池の場合には、作用極は光励起により起電力を生じる電極（例えば色素増感半導体電極）、2次電池の場合には、作用極（通常正極と呼ばれる）と対極（通常負極と呼ばれる）には酸化還元に伴いリチウムイオンを挿入放出しうる活物質が使用される。

【0065】【光電気化学電池】以下に、本発明の電解質組成物を利用した本発明の光電気化学電池について説

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明する。本発明の光電気化学電池は、導電性支持体上に、電解質組成物を含む電荷輸送層と、色素で増感された半導体を含む感光層と、対極とを有し、いわゆる以下に説明する光電変換素子を外部回路で仕事をさせるように構成したものである。本発明の光電気化学電池は、前記電荷輸送層が本発明の電解質組成物を含有しているので、光電変換性能に優れるとともに、経時での電池性能の劣化が小さい優れた耐久性を示す。

【0066】〔1〕光電変換素子

図1に、本発明に適用可能な光電変換素子の一例を示す。光電変換素子10は、導電層12、下塗り層14、感光層16、電荷輸送層18及び対極導電層20が順次積層してなる。感光層16は、色素dによって増感した半導体層24と、電荷輸送材料1とからなる。半導体層24は、半導体微粒子sからなる多孔性の層であり、半導体微粒子sの間には空隙が形成され、該空隙に電荷輸送材料1が浸透している。電荷輸送材料1は、電荷輸送層18に用いる材料と同じ成分からなる。導電層12の下には基板26、及び対極導電層20の上には基板28が配置されている。基板26、28は光電変換素子に強度を付与するためのものであり、なくてもよい。また、それぞれの層の境界、例えば、導電層12と感光層16との境界、感光層16と電荷輸送層18との境界、電荷輸送層18と対極導電層20との境界等では、各層の構成成分同士が相互に拡散混合していてもよい。尚、光電変換素子10には、いずれか又は双方から光を入射してもよく、光を入射する側の導電層12と基板26及び／又は対極導電層20と基板28を、それぞれ光透過性を有する材料から構成することができる。

【0067】次に、光電変換素子10の作用について説明する。尚、半導体微粒子sがn型である場合について説明する。光電変換素子10に光が入射すると、入射した光は感光層16に達し、色素d等によって吸収され、励起状態の色素dを生成する。励起された色素d等は、高エネルギーの電子を半導体微粒子sの伝導帯に渡し、自らは酸化体となる。前記伝導帯に移った電子は半導体微粒子sのネットワークにより導電層12に到達する。従って、導電層12は対極導電層20に対して負の電位を持つ。光電変換素子10を光電池に利用した態様では、この光電池を外部回路につなぐと、導電層12中の電子は外部回路で仕事をしながら対極導電層20に達する。電子は、電荷輸送材料が電解質である場合は、この電解質成分（例えば I^- ）を還元するとともに、生成した還元体（例えば I_2 ）が色素dの酸化体を還元して元に戻す。光を照射し続けることにより、一連の反応が引き続き起こり、電気を取り出すことができる。

【0068】以下、前記光電変換素子の各層に使用可能な材料及びその形成方法について説明する。尚、以下で、「導電性支持体」というときは、導電層12のみ、及び導電層12と任意で設ける基板26からなるものの

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双方を含み、「対極」というときは、対極導電層20のみ、及び対極導電層20と任意で設ける基板28からなるものの双方を含む。

【0069】(A)導電性支持体

導電性支持体は、(1)導電層の単層、又は(2)導電層及び基板の2層からなる。(1)の場合は、導電層として強度や密封性が十分に保たれるような材料が使用され、例えば、金属材料(白金、金、銀、銅、亜鉛、チタン、アルミニウム等又はこれらを含む合金)を用いることができる。(2)の場合、感光層側に導電剤を含む導電層を有する基板を使用することができる。好ましい導電剤としては金属(例えば白金、金、銀、銅、亜鉛、チタン、アルミニウム、インジウム等又はこれらを含む合金)、炭素、又は導電性金属酸化物(インジウム-スズ複合酸化物、酸化スズにフッ素又はアンチモンをドーブした等)が挙げられる。導電層の厚さは0.02~10 μ m程度が好ましい。

【0070】導電性支持体は表面抵抗が低い程よい。好ましい表面抵抗の範囲は50 Ω /□以下であり、さらに好ましくは20 Ω /□以下である。

【0071】導電性支持体側から光を照射する場合には、導電性支持体は実質的に透明であるのが好ましい。実質的に透明であるとは、可視~近赤外領域(400~1200nm)の光の一部又は全域において透過率が10%以上であることを意味し、50%以上であるのが好ましく、80%以上がより好ましい。特に、感光層が感度を有する波長域の透過率が高いことが好ましい。

【0072】透明導電性支持体としては、ガラス又はプラスチック等の透明基板の表面に導電性金属酸化物からなる透明導電層を塗布又は蒸着等により形成したものが好ましい。透明導電層として好ましいものは、フッ素もしくはアンチモンをドーピングした二酸化スズあるいはインジウム-スズ酸化物(ITO)である。透明基板には低コストと強度の点で有利なソーダガラス、アルカリ溶出の影響のない無アルカリガラスなどのガラス基板のほか、透明ポリマーフィルムを用いることができる。透明ポリマーフィルムの材料としては、トリアセチルセルロース(TAC)、ポリエチレンテレフタレート(PET)、ポリエチレンナフタレート(PEN)、シンジオタクチックポリスチレン(SPS)、ポリフェニレンスルフィド(PPS)、ポリカーボネート(PC)、ポリアリレート(PAr)、ポリスルホン(PSF)、ポリエステルスルホン(PES)、ポリイミド(PI)、ポリエーテルイミド(PEI)、環状ポリオレフィン、ブロム化フェノキシ等がある。十分な透明性を確保するために、導電性金属酸化物の塗布量はガラス又はプラスチックの支持体1m²当たり0.01~100gとするのが好ましい。

【0073】透明導電性支持体の抵抗を下げる目的で金属リードを用いるのが好ましい。金属リードの材質は、

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白金、金、ニッケル、チタン、アルミニウム、銅、銀等の金属が好ましい。金属リードは透明基板に蒸着、スパッタリング等で設置し、その上に導電性の酸化スズ又はITO膜からなる透明導電層を設けるのが好ましい。金属リード設置による入射光量の低下は、好ましくは10%以内、より好ましくは1~5%とする。

【0074】(B)感光層

前記感光層は、光を吸収して電荷分離を行い、電子と正孔を生ずる機能を有する。前記感光層は色素増感された半導体を含む。色素増感された半導体では、光吸収及びこれによる電子及び正孔の発生は主として色素において起こり、半導体はこの電子(又は正孔)を受け取り、伝達する役割を担う。本発明で用いる半導体は、光励起下で伝導電子がキャリアーとなり、アノード電流を与えるn型半導体であることが好ましい。

【0075】(1)半導体

半導体としては、シリコン、ゲルマニウムのような単体半導体、III-V系化合物半導体、金属のカルコゲナイド(例えば酸化物、硫化物、セレン化物、又はそれらの複合物等)、又はペロブスカイト構造を有する化合物(例えばチタン酸ストロンチウム、チタン酸カルシウム、チタン酸ナトリウム、チタン酸バリウム、ニオブ酸カリウム等)等を使用することができる。

【0076】好ましい金属のカルコゲナイドとして、チタン、スズ、亜鉛、鉄、タングステン、ジルコニウム、ハフニウム、ストロンチウム、インジウム、セリウム、イットリウム、ランタン、バナジウム、ニオブ、又はタンタルの酸化物、カドミウム、亜鉛、鉛、銀、アンチモン又はヒスマスの硫化物、カドミウム又は鉛のセレン化物、カドミウムのテルル化物等が挙げられる。他の化合物半導体としては、亜鉛、ガリウム、インジウム、カドミウム等のリン化物、ガリウム-ヒ素又は銅-インジウムのセレン化物、銅-インジウムの硫化物等が挙げられる。さらに、M_xO_yS_z又はM^x_xM^y_yO_z(M、M'及びM''はそれぞれ金属元素、Oは酸素原子、x、y及びzは価数が中性になる組み合わせの数)で表される複合物も好ましく用いることができる。

【0077】本発明に用いる半導体の好ましい具体例は、Si、TiO₂、SnO₂、Fe₂O₃、WO₃、ZnO、Nb₂O₅、CdS、ZnS、PbS、Bi₂S₃、CdSe、CdTe、SrTiO₃、GaP、InP、GaAs、CuInS₂、CuInSe₂等であり、より好ましくはTiO₂、ZnO、SnO₂、Fe₂O₃、WO₃、Nb₂O₅、CdS、PbS、CdSe、SrTiO₃、InP、GaAs、CuInS₂およびCuInSe₂であり、特に好ましくはTiO₂およびNb₂O₅であり、最も好ましくはTiO₂である。TiO₂はアナターゼ型結晶を70%以上含むTiO₂が好ましく、特に好ましくは100%アナターゼ型結晶のTiO₂である。また、これらの半導体中の電子導電性を上げる目的で、

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金属をドーブすることも有効である。ドーブする金属としては2価、3価の金属が好ましい。半導体から電荷輸送層へ逆電流が流れるのを防止する目的で、半導体に1価の金属をドーブすることも有効である。

【0078】本発明に用いる半導体は単結晶でも多結晶でもよいが、製造コスト、原材料確保、エネルギーペイバックタイム等の観点からは多結晶が好ましく、半導体微粒子からなる多孔質膜が特に好ましい。また、一部アモルファス部分を含んでいてもよい。

【0079】半導体微粒子の粒径は一般にnm~ μ mのオーダーであるが、投影面積を円に換算したときの直径から求めた一次粒子の平均粒径は5~200nmであるのが好ましく、8~100nmがより好ましい。また分散液中の半導体微粒子（二次粒子）の平均粒径は0.01~30 μ mが好ましい。粒径分布の異なる2種類以上の微粒子を混合してもよく、この場合、小さい粒子の平均サイズは25nm以下であるのが好ましく、より好ましくは10nm以下である。入射光を散乱させて光捕獲率を向上させる目的で、粒径の大きな、例えば100nm以上、300nm程度の半導体粒子を混合することも好ましい。

【0080】半導体微粒子の種類も異なる2種以上の混合であってもよい。2種以上の半導体微粒子を混合して使用する場合、1種はTiO₂、ZnO、Nb₂O₅、もしくはSrTiO₃であることが好ましい。またもう1種としてはSnO₂、Fe₂O₃、もしくはWO₃であることが好ましい。さらに好ましい組み合わせとしては、ZnOとSnO₂、ZnOとWO₃又はZnO、SnO₂とWO₃などの組み合わせを挙げることができる。2種以上の半導体微粒子を混合して用いる場合、それぞれの粒径が異なってもよい。特に上記1種目で挙げた半導体微粒子の粒径が大きく、2種目以降で挙げた半導体微粒子が小さい組み合わせが好ましい。好ましくは大きい粒径の粒子が100nm以上で、小さい粒径の粒子が15nm以下の組み合わせである。

【0081】半導体微粒子の作製法としては、作花済夫の「ゾルーゲル法の科学」アグネ承風社（1998年）、技術情報協会の「ゾルーゲル法による薄膜コーティング技術」（1995年）等に記載のゾルーゲル法、杉本忠夫の「新合成法ゲル-ゾル法による単分散粒子の合成とサイズ形態制御」、まてりあ、第35巻、第8号、1012~1018頁（1996年）に記載のゲル-ゾル法が好ましい。またDegussa社が開発した塩化物を酸水素塩中で高温加水分解により酸化物を作製する方法も好ましい。

【0082】半導体微粒子が酸化チタンの場合、上記ゾルーゲル法、ゲル-ゾル法、塩化物の酸水素塩中で高温加水分解法はいずれも好ましいが、さらに清野学の「酸化チタン物性と応用技術」技報堂出版（1997年）に記載の硫酸法及び塩素法を用いることもできる。

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さらにゾルーゲル法として、Barbeらのジャーナル・オブ・アメリカン・セラミック・ソサエティー、第80巻、第12号、3157~3171頁（1997年）に記載の方法や、Burnsideらのケミストリー・オブ・マテリアルズ、第10巻、第9号、2419~2425頁に記載の方法も好ましい。

【0083】（2）半導体微粒子層

前記半導体は、例えば、前記導電性支持体上に形成された半導体微粒子層の形態で使用される。半導体微粒子を導電性支持体上に塗布するには、半導体微粒子の分散液又はコロイド溶液を導電性支持体上に塗布する方法の他に、前述のゾルーゲル法等を使用することもできる。光電変換素子の製造化、半導体微粒子液の物性、導電性支持体の融通性等を考慮した場合、湿式の製膜方法が比較的利益である。湿式の製膜方法としては、塗布法、印刷法、電解析出法及び電着法が代表的である。また、金属を酸化する方法、金属溶液から配位子交換等で液相にて析出させる方法（LPD法）、スパッタ等で蒸着する方法、CVD法、あるいは加温した基板上に熱分解する金属酸化物プレカーサーを吹き付けて金属酸化物を形成するSPD法を利用することもできる。

【0084】半導体微粒子の分散液を作製する方法としては、前述のゾルーゲル法の他に、乳鉢ですり潰す方法、ミルを使って粉砕しながら分散する方法、あるいは半導体を合成する際に溶媒中で微粒子として析出させそのまま使用する方法等が挙げられる。

【0085】分散媒としては、水又は各種の有機溶媒（例えばメタノール、エタノール、イソプロピルアルコール、シトロネロール、ターピネオール、ジクロロメタン、アセトン、アセトニトリル、酢酸エチル等）が挙げられる。分散の際、必要に応じて、例えばポリエチレングリコール、ヒドロキシエチルセルロース、カルボキシメチルセルロースのようなポリマー、界面活性剤、酸、又はキレート剤等を分散助剤として用いてもよい。ポリエチレングリコールの分子量を変えることで、分散液の粘度が調整可能となり、さらに剥がれにくい半導体層を形成したり、半導体層の空隙率をコントロールできるので、ポリエチレングリコールを添加することは好ましい。

【0086】塗布方法としては、アプリケーション系としてローラ法、ディップ法等、メータリング系としてエアナイフ法、ブレード法等、またアプリケーションとメータリングを同一部分にできるものとして、特公昭58-4589号に開示されているワイヤーバー法、米国特許2681294号、同2761419号、同2761791号等に記載のスライドホッパー法、エクストルージョン法、カーテン法等が好ましい。また汎用機としてスピン法やスプレー法も好ましい。湿式印刷方法としては、凸版、オフセット及びグラビアの3大印刷法をはじめ、凹版、ゴム版、スクリーン印刷等が好ましい。こ

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れらの中から、液粘度やウェット厚さに応じて、好ましい製膜方法を選択する。

【0087】半導体微粒子の層は単層に限らず、粒径の違った半導体微粒子の分散液を多層塗布したり、種類が異なる半導体微粒子（あるいは異なるバインダー、添加剤）を含有する塗布層を多層塗布したりすることもできる。一度の塗布で膜厚が不足の場合にも多層塗布は有効である。

【0088】一般に半導体微粒子層の厚さ（感光層の厚さと同じ）が厚くなるほど単位投影面積当たりの担持色素量が増えるため、光の捕獲率が高くなるが、生成した電子の拡散距離が増すため電荷再結合によるロスも大きくなる。したがって、半導体微粒子層の好ましい厚さは0.1~100 μmである。光電池に用いる場合、半導体微粒子層の厚さは1~30 μmが好ましく、2~25 μmがより好ましい。半導体微粒子の支持体1m²当たりに対する塗布量は、0.5~100 gが好ましく、3~50 gがより好ましい。

【0089】半導体微粒子を導電性支持体上に塗布した後で半導体微粒子同士を電子的に接触させるとともに、塗膜強度の向上や支持体との密着性を向上させるために、加熱処理するのが好ましい。好ましい加熱温度の範囲は40℃以上70℃以下であり、より好ましくは100℃以上600℃以下である。また加熱時間は10分~10時間程度である。ポリマーフィルムのように融点や軟化点の低い支持体を用いる場合、高温処理は支持体の劣化を招くため、好ましくない。またコストの観点からでもできる限り低温（例えば50~350℃）であるのが好ましい。低温化は、5 nm以下の小さい半導体微粒子や酸、金属酸化物プレカーサーの存在下での加熱処理等により可能となり、また、紫外線、赤外線、マイクロ波等の照射や電界、超音波を印加することにより行うこともできる。同時に不要な有機物を除去する目的で、上記の照射や印加のほか加熱、減圧、酸素プラズマ処理、純水洗浄、溶剤洗浄、ガス洗浄等を適宜組み合わせ併用することが好ましい。

【0090】加熱処理後、半導体微粒子の表面積を増大させたり、半導体微粒子近傍の純度を高め、色素から半導体微粒子への電子注入効率を高める目的で、例えば四塩化チタン水溶液を用いた化学メッキ処理や三塩化チタン水溶液を用いた電気化学的メッキ処理を行ってもよい。また、半導体微粒子から電荷輸送層へ逆電流が流れるのを防止する目的で、粒子表面に色素以外の電子導性の低い有機物を吸着させることも有効である。吸着させる有機物としては疎水性基を有する物が好ましい。

【0091】半導体微粒子層は、多くの色素を吸着することができるように大きい表面積を有することが好ましい。半導体微粒子の層を支持体上に塗布した状態で表面積は、投影面積に対して10倍以上であるのが好ましく、さらに100倍以上であるのが好ましい。この上限

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は特に制限はないが、通常1000倍程度である。

【0092】(3) 色素

感光層に用いる増感色素は、可視域や近赤外域に吸収を有し、半導体を増感し得る化合物なら任意に用いることができ、有機金属錯体色素、メチン色素、ポルフィリン系色素およびフタロシアニン系色素が好ましい。また、光電変換の波長域をできるだけ広くし、かつ変換効率を上げるため、二種類以上の色素を併用又は混合することができる。この場合、目的とする光源の波長域と強度分布に合わせるように、併用又は混合する色素とその割合を選ぶことができる。

【0093】こうした色素は、半導体微粒子の表面に対して吸着能力の有る適当な結合基（interlocking group）を有しているのが好ましい。好ましい結合基としては、COOH基、OH基、SO₃H基、-P(O)(OH)₂基および-OP(O)(OH)₂基のような酸性基、あるいはオキシム、ジオキシム、ヒドロキシキノリン、サリチレート又はα-ケトエノレートのようなπ伝導性を有するキレート化基が挙げられる。なかでもCOOH基、-P(O)(OH)₂基および-OP(O)(OH)₂基が特に好ましい。これらの基はアルカリ金属等と塩を形成していてもよく、また分子内塩を形成していてもよい。またポリメチン色素の場合、メチン錯がスクアリウム環やクロコニウム環を形成する場合のように酸性基を含有する場合、この部分を結合基として有していてもよい。

【0094】以下、感光層に用いる好ましい増感色素を具体的に説明する。

(a) 有機金属錯体色素

色素が金属錯体色素である場合、金属フタロシアニン色素、金属ポルフィリン色素およびルテニウム錯体色素が好ましく、ルテニウム錯体色素が特に好ましい。ルテニウム錯体色素としては、例えば米国特許4927721号、同4684537号、同5084365号、同5350644号、同5463057号、同5525440号等の各明細書、及び、特開平7-249790号、特表平10-504512号、世界特許98/50393号、特開2000-26487号等の各公報に記載の錯体色素が挙げられる。

【0095】さらに前記色素がルテニウム錯体色素である場合、下記一般式(IV)で表されるルテニウム錯体色素が好ましい。

一般式(IV)

(A¹), Ru(B-a), (B-b), (B-c),

前記一般式(IV)中、A¹は1又は2座の配位子を表す。A¹はCl, SCN, H₂O, Br, I, CN, NC O, SeCN, α-ジケトン類、シュウ酸及びジチオカルバミン酸の誘導体からなる群から選ばれる配位子であるのが好ましい。1が2以上の場合、2以上のA¹は同一でも異なってもよい。前記一般式(IV)中、B

(15)

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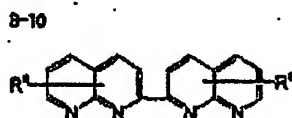
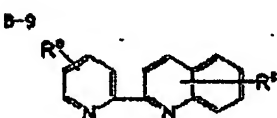
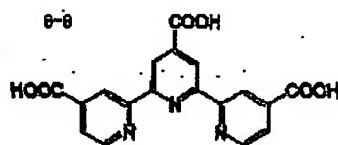
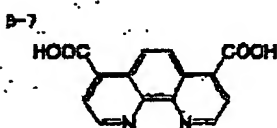
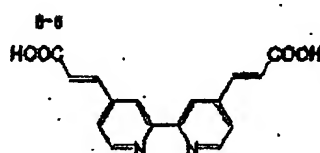
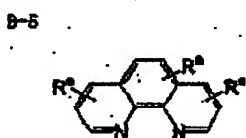
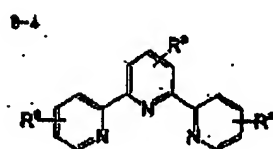
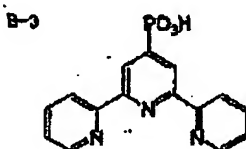
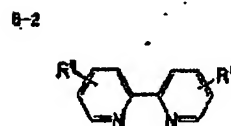
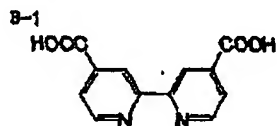
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-a. B-b及びB-cは、それぞれ独立に下記式(B-1)~(B-10)のいずれかで表される配位子を表す。tは0~3のいずれかの整数を表し、u、v及びwは各々0又は1を表し、前記一般式(IV)で表される*

*ルテニウム錯体が6配位錯体となる様に、配位子の種類に応じて適宜組み合わされる。

[0096]

[化12]



【0097】前記式(B-1)~(B-10)中、R^uは水素原子又は置換基を表し、該置換基としては、例えば、ハロゲン原子、炭素原子数1~12の置換又は無置換のアルキル基、炭素原子数7~12の置換又は無置換のアラルキル基、炭素原子数6~12の置換又は無置換のアリール基、酸性基(これらの酸性基は塩を形成してもよい)又はキレート化基が挙げられる。アルキル基及びアラルキル基のアルキル部分は直鎖状でも分岐状でもよい。また、前記アリール基及びアラルキル基のア

リール部分は単環でも多環(縮合環、環集合)でもよい。前記一般式(IV)中、B-a、B-b及びB-cは同一でも異なってもよい。

【0098】有機金属錯体色素の好ましい具体例(例示化合物R-1~17)を以下に示すが、本発明に用いられる色素は以下の具体例に限定されるものではない。

40 【0099】

[化13]

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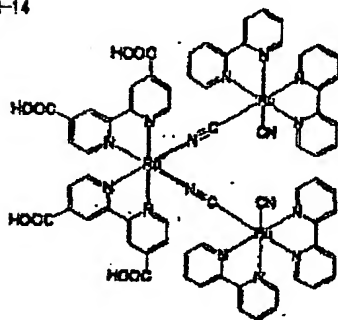
 $(A^1)_pRu(B-a)(B-b)(B-c)$

	A ¹	p	B-a	B-b	B-c	R ^A
R-1	SCN	2	B-1	B-1	-	-
R-2	CN	2	B-1	B-1	-	-
R-3	Cl	2	B-1	B-1	-	-
R-4	CN	2	B-7	B-7	-	-
R-5	SCN	2	B-7	B-7	-	-
R-6	SCN	2	B-1	B-2	-	H
R-7	SCN	1	B-1	B-3	-	-
R-8	Cl	1	B-1	B-4	-	H
R-9	I	2	B-1	B-5	-	H
R-10	SCN	3	B-8	-	-	-
R-11	CN	3	B-8	-	-	-
R-12	SCN	1	B-2	B-8	-	H
R-13	-	0	B-1	B-1	B-1	-

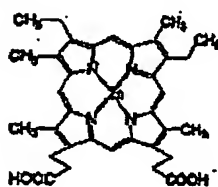
[0100]

* * [化14]

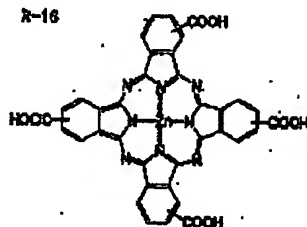
R-14



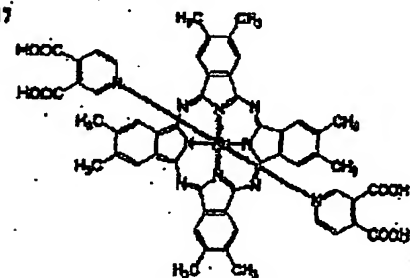
R-15



R-16



R-17



[0101] (b) メチン色素

本発明に使用する好ましいメチン色素は、シアニン色

素、メロシアニン色素、スクワリウム色素などのポリ

50 メチン色素である。本発明で好ましく用いられるポリメ

(17)

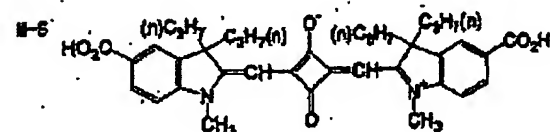
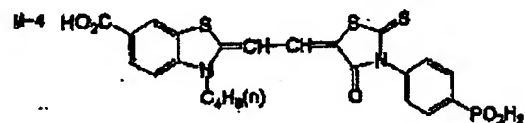
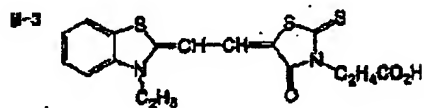
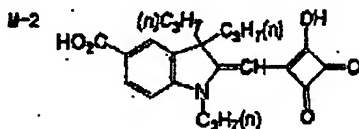
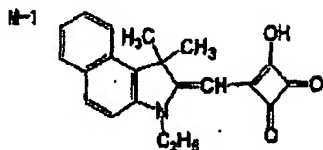
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チン色素としては、例えば、特開平11-35836号、特開平11-67285号、特開平11-86916号、特開平11-97725号、特開平11-158395号、特開平11-163378号、特開平11-214730号、特開平11-214731号、特開平11-238905号、特開2000-26487号、*

*欧州特許892411号、同911841号及び同991092号の各明細書に記載の色素が挙げられる。好ましいメチン色素の具体例を以下に示す。
[0102]
[化15]



[0103]

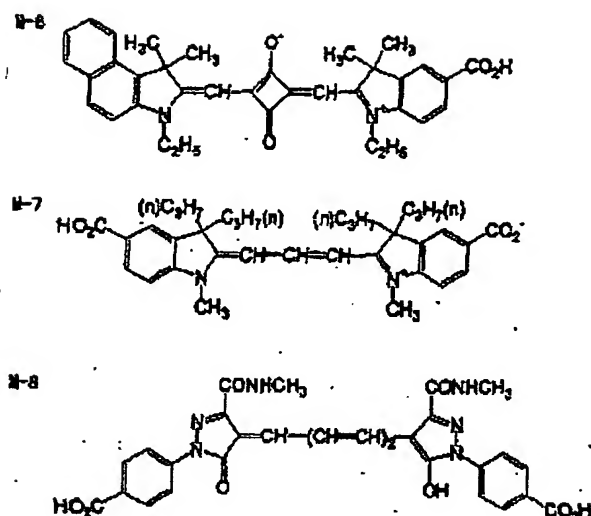
[化16]

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【0104】(4) 半導体微粒子への色素の吸着

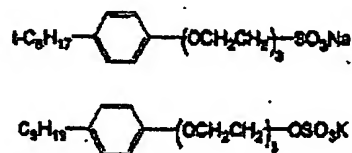
半導体微粒子に色素を吸着させるには、色素の溶液中に
 良く乾燥した半導体微粒子層を有する導電性支持体を浸
 漬するか、色素の溶液を半導体微粒子層に塗布する方法
 を用いることができる。前者の場合、浸漬法、ディップ
 法、ローラ法、エアナイフ法等が使用可能である。浸
 漬法の場合、色素の吸着は室温で行ってもよいし、特開
 平7-249790号に記載されているように加熱処理
 して行ってもよい。また後者の塗布方法としては、ワイ
 ヤーバー法、スライドホッパー法、エクストルージョン
 法、カーテン法、スピン法、スプレー法等がある。色素
 を溶解する溶媒として好ましいのは、例えば、アルコール
 類（メタノール、エタノール、1-ブタノール、ベン
 ジルアルコール等）、ニトリル類（アセトニトリル、ブ
 ロピオニトリル、3-メトキシブピオニトリル等）、
 ニトロメタン、ハロゲン化炭化水素（ジクロロメタン、
 ジクロロエタン、クロロホルム、クロロベンゼン等）、
 エーテル類（ジエチルエーテル、テトラヒドロフラン
 等）、ジメチルスルホキシド、アミド類（N、N-ジメ
 チルホルムアミド、N、N-ジメチルアセタミド等）、
 N-メチルピロリドン、1、3-ジメチルイミダゾリジ
 ノン、3-メチルオキサゾリジノン、エステル類（酢酸
 エチル、酢酸ブチル等）、炭酸エステル類（炭酸ジエチ
 ル、炭酸エチレン、炭酸プロピレン等）、ケトン類（ア
 セトン、2-ブタノン、シクロヘキサノン等）、炭化水
 素（ヘキサン、石油エーテル、ベンゼン、トルエン等）
 やこれらの混合溶媒が挙げられる。

【0105】色素の全吸着量は、多孔質半導体電極基板
 の単位表面積（1m²）当たり0.01~100mmol
 が好ましい。また色素の半導体微粒子に対する吸着量
 は、半導体微粒子1g当たり0.01~1mmolの範
 囲であるのが好ましい。前記範囲の色素吸着量とするこ

とにより半導体における増感効果が十分に得られる。こ
 れに対し、色素が少なすぎると増感効果が不十分とな
 り、また色素が多すぎると半導体に付着していない色素
 が浮遊し、増感効果を低減させる原因となる。色素の吸
 着量を増大させるためには、吸着前に加熱処理を行うの
 が好ましい。加熱処理後、半導体微粒子表面に水が吸着
 するのを避けるため、常温に戻さず、半導体電極基板
 の温度が60~150℃の間で素早く色素の吸着操作を
 行うのが好ましい。また、色素間の凝集などの相互作用
 を低減する目的で、無色の化合物を色素に添加し、半導
 体微粒子に共吸着させてもよい。この目的で有効な化合
 物は界面活性性性質、構造をもった化合物であり、例え
 ば、カルボキシル基を有するステロイド化合物（例えば
 ケノデオキシコール酸）や下記の例のようなスルホン酸
 塩類が挙げられる。

【0106】

【化17】



【0107】未吸着の色素は、吸着後速やかに洗浄によ
 り除去するのが好ましい。湿式洗浄槽を使い、アセトニ
 トリル等の極性溶剤、アルコール系溶剤のような有機溶
 媒で洗浄を行うのが好ましい。色素を吸着した後にはアミ
 ン類や4級塩を用いて半導体微粒子の表面を処理しても
 よい。好ましいアミン類としては、ピリジン、4-1-
 プチルピリジン及びポリビニルピリジン等が挙げられ、
 好ましい4級塩としては、テトラブチルアンモニウムヨ
 ーゾド及びテトラヘキシルアンモニウムヨーゾド等が挙

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げられる。これらが液体の場合はそのまま用いてもよいし、有機溶媒に溶解して用いてもよい。

【0108】(C) 電荷輸送層

電荷輸送層は、色素の酸化体に電子を補充する機能を有する電荷輸送材料を含有する層である。この電荷輸送層に用いることのできる代表的な電荷輸送材料の例としては、(i) イオン輸送材料として、酸化還元対のイオンが溶解した溶液(電解液)、酸化還元対の溶液をポリマーマトリックスのゲルに含浸したいわゆるゲル電解質、酸化還元対イオンを含有する溶融塩電解質、さらには固体電解質が挙げられる。また、イオンがかかわる電荷輸送材料のほかに、(ii) 固体中のキャリア移動がかかわる電荷輸送材料として、電子輸送材料や正孔(ホール)輸送材料を用いることもできる。本発明では、この電荷輸送層に本発明の電解質組成物を使用するが、これ以外の上記電荷輸送材料を併用することもできる。

【0109】(1) 電荷輸送層の形成

電荷輸送層の形成方法に関しては2通りの方法が考えられる。1つは感光層の上に先に対極を貼り合わせておき、その間隙に液状の電荷輸送層を挟み込む方法である。もう1つは感光層上に直接、電荷輸送層を付与する方法で、対極はその後付与することになる。

【0110】前者の場合、電荷輸送層の挟み込み方法として、浸漬等による毛管現象を利用する常圧プロセス、又は常圧より低い圧力にして間隙の気相を液相に置換する真空プロセスを利用できる。

【0111】後者の場合、湿式の電荷輸送層においては未乾燥のまま対極を付与し、エッジ部の液漏れ防止措置を施すことになる。またゲル電解質の場合には、湿式で塗布して重合等の方法により固体化する方法があり、その場合には乾燥、固定化した後に対極を付与することもできる。電解液のほか湿式有機正孔輸送材料やゲル電解質を付与する方法としては、前述の半導体微粒子層や色素の付与と同様の方法を利用できる。

【0112】(D) 対極

対極は前記の導電性支持体と同様に、導電性材料からなる対極導電層の単層構造でもよいし、対極導電層と支持基板から構成されていてもよい。対極導電層に用いる導電材としては、金属(例えば白金、金、銀、銅、アルミニウム、マグネシウム、インジウム等)、炭素、又は導電性金属酸化物(インジウムスズ複合酸化物、フッ素ドープ酸化スズ等)が挙げられる。この中でも白金、金、銀、銅、アルミニウム、マグネシウムを対極導電層として好ましく使用することができる。対極の好ましい支持基板の例は、ガラス又はプラスチックであり、これに上記の導電剤を塗布又は蒸着して用いる。対極導電層の厚さは特に制限されないが、 $3\text{ nm} \sim 10\text{ }\mu\text{m}$ が好ましい。対極導電層の表面抵抗は低い程よい。好ましい表面抵抗の範囲としては $50\text{ }\Omega/\square$ 以下であり、さらに好ましくは $20\text{ }\Omega/\square$ 以下である。

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【0113】導電性支持体と対極のいずれか一方又は両方から光を照射してよいので、感光層に光が到達するためには、導電性支持体と対極の少なくとも一方が実質的に透明であればよい。発電効率の向上の観点からは、導電性支持体を透明にして、光を導電性支持体側から入射させるのが好ましい。この場合、対極は光を反射する性質を有するのが好ましい。このような対極としては、金属又は導電性の酸化物を蒸着したガラス又はプラスチック、あるいは金属薄膜を使用できる。

【0114】対極は、電荷輸送層上に直接導電材を塗布、メッキ又は蒸着(PVD、CVD)するか、対極導電層を有する基板の対極導電層側を貼り付けねばよい。また、導電性支持体の場合と同様に、特に対極が透明の場合には、対極の抵抗を下げる目的で金属リードを用いるのが好ましい。なお、好ましい金属リードの材質及び設置方法、金属リード設置による入射光量の低下等は、導電性支持体の場合と同じである。

【0115】(E) その他の層

対極と導電性支持体の短絡を防止するため、予め導電性支持体と感光層との間に緻密な半導体の薄膜層を下塗り層として塗設しておくことが好ましく、電荷輸送層に電子輸送材料や正孔輸送材料を用いる場合は、特に有効である。下塗り層として好ましいのは TiO_2 、 SnO_2 、 Fe_2O_3 、 WO_3 、 ZnO 、 Nb_2O_5 であり、さらに好ましくは TiO_2 である。下塗り層は、例えばElectrochim. Acta 40, 643-652(1995)に記載されているスプレーバヨリシス法、スパッタ法等により塗設することができる。下塗り層の好ましい膜厚は $5 \sim 1000\text{ nm}$ であり、 $10 \sim 500\text{ nm}$ がさらに好ましい。

【0116】また、電極として作用する導電性支持体と対極の一方又は両方の外側表面、導電層と基板の間又は基板の中間に、保護層、反射防止層等の機能性層を設けてもよい。これらの機能性層の形成には、その材質に応じて塗布法、蒸着法、貼り付け法等を用いることができる。

【0117】本発明の光電気化学電池は、前記した各々の構成物の劣化や内容物の揮散を防止するために、側面をポリマーや接着剤等で密封するのが好ましい。

【0118】本発明の光電気化学電池は、基本的に前記光電変換素子と同様の構成であり、前記光電変換素子をリード線を介して外部回路に接続し、外部回路で仕事をさせるように構成したものである。前記導電性支持体及び前記対極にリード線を介して接続される外部回路自体は、公知のものを使用できる。また、本発明の光電気化学電池は、従来の太陽電池モジュールと基本的には同様のモジュール構造をとり得る。前記太陽電池モジュールは、一般的には金属、セラミック等の支持基板の上にセルが構成され、その上を充填樹脂や保護ガラス等で覆い、支持基板の反対側から光を取り込む構造をとる

50 が、支持基板に強化ガラス等の透明材料を用い、その上

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にセルを構成してその透明の支持基板側から光を取り込む構造とすることも可能である。具体的には、スーパーストレートタイプ、サブストレートタイプ、ポッティングタイプと呼ばれるモジュール構造、アモルファスシリコン太陽電池などで用いられる基板一体型モジュール構造等が知られており、本発明の光電気化学電池も使用目的や使用場所及び環境により、適宜これらのモジュール構造を選択できる。具体的には、特開2000-268892号公報に記載の構造や態様を適用することが好ましい。

【0119】〔非水二次電池〕以下に、本発明の電解質組成物を利用した本発明の非水二次電池について説明する。本発明の非水二次電池は、本発明の電解質組成物を含むことを特徴とする。本発明の非水二次電池は、本発明の電解質組成物を含有しているので、容量を大きく低下させることなく、優れたサイクル性を示す。

【0120】本発明の電解質組成物を非水二次電池に用いる場合、正極活物質は可逆的にリチウムイオンを挿入・放出できる遷移金属酸化物でもよいが、特にリチウム含有遷移金属酸化物が好ましい。本発明で用いられる好ましいリチウム含有遷移金属酸化物正極活物質としては、リチウム含有Ti、V、Cr、Mn、Fe、Co、Ni、Cu、Mo、Wを含む酸化物が挙げられる。またリチウム以外のアルカリ金属（周期律表の第1（IA）族、第2（IIA）族の元素）、及び／又はAl、Ga、In、Ge、Sn、Pb、Sb、Bi、Si、P、Bなどを混合してもよい。混合量は遷移金属に対して0～30mol％が好ましい。

【0121】本発明で用いられるより好ましいリチウム含有遷移金属酸化物正極活物質としては、リチウム化合物／遷移金属化合物（ここで遷移金属とは、Ti、V、Cr、Mn、Fe、Co、Ni、Mo、Wから選ばれる少なくとも1種）の合計のモル比が0.3～2.2になるように混合して合成することが好ましい。

【0122】本発明で用いられる特に好ましいリチウム含有遷移金属酸化物正極活物質としては、リチウム化合物／遷移金属化合物（ここで遷移金属とは、V、Cr、Mn、Fe、Co、Niから選ばれる少なくとも1種）の合計のモル比が0.3～2.2になるように混合して合成することが好ましい。

【0123】本発明で用いられる特に好ましいリチウム含有遷移金属酸化物正極活物質は、 $\text{Li}_x\text{M}'\text{O}_2$ （ M' はCo、Ni、Fe及びMnから選ばれる1種以上、 $g=0\sim1.2$ ）を含む材料。又は $\text{Li}_x\text{M}'\text{O}_2$ （ M' はMn、 $h=0\sim2$ ）で表されるスピネル構造を有する材料であり、 M' 及び M'' としては遷移金属以外にAl、Ga、In、Ge、Sn、Pb、Sb、Bi、Si、P又はBなどを混合してもよい。混合量は遷移金属に対して0～30mol％が好ましい。

【0124】本発明で用いられる最も好ましいリチウム

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含有遷移金属酸化物正極活物質としては、 Li_xCoO_2 、 Li_xNiO_2 、 Li_xMnO_2 、 $\text{Li}_x\text{Co}_y\text{Ni}_{1-y}\text{O}_2$ 、 $\text{Li}_x\text{Mn}_h\text{O}_2$ （ここで $g=0.02\sim1$ 、 2 、 $y=0.1\sim0.9$ 、 $h=0\sim2$ ）が挙げられる。ここで、上記の g 値は、充放電開始前の値であり、充放電により増減する。

【0125】正極活物質は、リチウム化合物と遷移金属化合物を混合、焼成する方法や溶液反応など、公知の方法により合成することができるが、特に焼成法が好ましい。

【0126】本発明で用いる正極活物質の平均粒子サイズは特に限定されないが、0.1～50 μm が好ましい。比表面積としては特に限定されないが、BET法で0.01～50 m^2/g が好ましい。また正極活物質5gを蒸留水100mlに溶かした時の上澄み液のpHとしては7以上12以下が好ましい。

【0127】所定の粒子サイズにするには、よく知られた粉碎機や分級機を用いることができる。例えば、乳鉢、ボールミル、振動ボールミル、振動ミル、衛星ボールミル、遊星ボールミル、旋回気流型ジェットミルや篩などが用いられる。焼成によって得られた正極活物質は、水、酸性水溶液、アルカリ性水溶液、有機溶剤にて洗浄した後使用してもよい。

【0128】本発明で用いられる負極活物質の一つは、リチウムの吸蔵放出が可能な炭素質材料である。炭素質材料とは、実質的に炭素からなる材料である。例えば、石油ピッチ、天然黒鉛、気相成長黒鉛等の人造黒鉛、及びPAN系の樹脂やフルフルリアルコール樹脂等の各種の合成樹脂を焼成した炭素質材料を挙げることができる。さらに、PAN系炭素繊維、セルロース系炭素繊維、ピッチ系炭素繊維、気相成長炭素繊維、脱水PVA系炭素繊維、リグニン炭素繊維、ガラス状炭素繊維、活性炭素繊維等の各種炭素繊維類、メソフェーズ微小球体、グラファイトウィスカー、平板状の黒鉛等を挙げることができる。これらの炭素質材料は、黒鉛化の程度により難黒鉛化炭素材料と黒鉛系炭素材料に分けることもできる。また炭素質材料は、特開昭62-22066号公報、特開平2-6856号公報、同3-45473号公報に記載される面間隔や密度、結晶子の大きさを有することが好ましい。炭素質材料は、単一の材料である必要はなく、特開平5-90844号公報記載の天然黒鉛と人造黒鉛の混合物、特開平6-4516号公報記載の被覆層を有する黒鉛等を用いることもできる。

【0129】本発明に使用可能な負極活物質の他の例としては、酸化物、及び／又はカルコゲナイドが挙げられる。特に非晶質酸化物、及び／又はカルコゲナイドが好ましい。ここでいう「非晶質」とは $\text{CuK}\alpha$ 線を用いたX線回折法で 2θ 値で 20° から 40° の領域に頂点を有するブロードな散乱帯を有する物であり、結晶性の回折線を有してもよい。好ましくは 2θ 値で 40° 以上7

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0°以下に見られる結晶性の回折線のうち最も強い強度が、2θ値で20°以上40°以下に見られるブロードな散乱帯の頂点の回折強度の100倍以下であり、さらに好ましくは5倍以下であり、特に好ましくは、結晶性の回折線を有さないことである。

【0130】本発明では中でも半金属元素の非晶質酸化物、及び／又はカルコゲナイトが好ましく、周期律表第13(IIIB)族～15(VB)族の元素、Al、Ga、Si、Sn、Ge、Pb、Sb、Biの単独あるいはそれらの2種以上の組み合わせからなる酸化物、カルコゲナイトが選ばれる。

【0131】例えば、Ga₂O₃、SiO₂、GeO₂、SnO₂、PbO、PbO₂、Pb₂O₃、Pb₂O₄、Pb₃O₄、Sb₂O₃、Sb₂O₄、Sb₂O₅、Bi₂O₃、Bi₂O₅、SnSiO₃、GeS₂、SnS₂、SnS₃、PbS₂、PbS₃、Sb₂S₃、Sb₂S₅、SnS_{1.5}S_{2.5}などが好ましい。また、これらは、酸化リチウムとの複合酸化物、例えば、Li₂SnO₃であってもよい。

【0132】本発明における負極材料においては、Sn、Si、Geを中心とする非晶質酸化物がさらに好ましく、中でも下記一般式(V)で表される非晶質酸化物であることが好ましい。

一般式(V)

SnM^d₁M^e₂O_f

一般式(V)中、M^dは、Al、B、P及びGeから選ばれる少なくとも一種以上の元素を表し、M^eは周期律表第1(IA)族元素、第2(IIA)族元素、第3(IIIA)族元素及びハロゲン元素から選ばれる少なくとも一種以上の元素を表し、dは0.2以上2以下の数字、eは0.01以上1以下の数字で0.2<d+e<2、fは1以上6以下の数字を表す。

【0133】Snを主体とする非晶質酸化物としては、例えば次の化合物が挙げられるが、本発明はこれらに限定されるわけではない。

- C-1 SnSiO₃
- C-2 Sn_{0.5}Al_{0.5}B_{0.5}P_{0.5}Si_{1.5}O_{3.5}
- C-3 SnAl_{0.5}B_{0.5}Cs_{0.5}P_{0.5}O_{3.5}
- C-4 SnAl_{0.5}B_{0.5}Mg_{0.5}P_{0.5}O_{3.5}
- C-5 SnAl_{0.5}B_{0.5}Ba_{0.5}P_{0.5}O_{3.5}
- C-6 SnAl_{0.5}B_{0.5}Ba_{0.5}Mg_{0.5}P_{0.5}O_{3.5}
- C-7 SnAl_{0.5}B_{0.5}Ca_{0.5}P_{0.5}Si_{1.5}O_{3.5}
- C-8 SnAl_{0.5}B_{0.5}Si_{1.5}O_{3.5}
- C-9 SnAl_{0.5}B_{0.5}Mg_{0.5}P_{0.5}Si_{1.5}O_{3.5}
- C-10 SnAl_{0.5}B_{0.5}P_{0.5}Si_{1.5}O_{3.5}
- C-11 SnAl_{0.5}B_{0.5}P_{0.5}Si_{1.5}O_{3.5}
- C-12 SnAl_{0.5}B_{0.5}P_{0.5}Si_{1.5}O_{3.5}
- C-13 SnAl_{0.5}B_{0.5}Ba_{0.5}P_{0.5}Si_{1.5}O_{3.5}

- C-14 SnAl_{0.5}B_{0.5}Ca_{0.5}P_{0.5}Si_{1.5}O_{3.5}
- C-15 SnAl_{0.5}B_{0.5}Mg_{0.5}Si_{1.5}O_{3.5}
- C-16 SnAl_{0.5}B_{0.5}P_{0.5}Si_{1.5}O_{3.5}
- C-17 SnB_{0.5}K_{0.5}P_{0.5}Si_{1.5}O_{3.5}
- C-18 SnB_{0.5}F_{0.5}Mg_{0.5}P_{0.5}O_{3.5}

【0134】本発明における非晶質酸化物、及び／又はカルコゲナイトは、焼成法、溶液法いずれの方法も採用することができるが、焼成法がより好ましい。焼成法では、それぞれ対応する元素の酸化物、カルコゲナイトあるいは化合物をよく混合した後、焼成して非晶質酸化物及び／又はカルコゲナイトを得るのが好ましい。これらは、既に公知の方法により作製できる。

【0135】本発明に用いられる負極材料の平均粒子サイズは0.1～60μmが好ましい。所定の粒子サイズにするには、よく知られた粉碎機や分級機が用いられる。例えば、乳鉢、ボールミル、サンドミル、振動ボールミル、衛星ボールミル、遊星ボールミル、旋回気流型ジェットミルや篩などが用いられる。粉碎時には水、あるいはメタノール等の有機溶媒を共存させた湿式粉碎も必要に応じて行うことができる。所望の粒径とするためには分級を行うことが好ましい。分級方法としては特に限定はなく、篩、風力分級機などを必要に応じて用いることができる。分級は乾式、湿式ともに用いることができる。

【0136】本発明において、Sn、Si、Geを中心とする非晶質酸化物負極材料に併せて用いることができる負極材料としては、リチウムイオン又はリチウム金属を吸蔵・放出できる炭素材料や、リチウム、リチウム合金、リチウムと合金可能な金属が挙げられる。

【0137】本発明に用いられる電解液には、導電剤、結着剤やフィラーなどの他に、非プロトン性有機溶媒が添加される。

【0138】前記導電剤は、構成された電池において、化学変化を起こさない電子伝導性材料であれば何でもよい。通常、天然黒鉛（鱗状黒鉛、鱗片状黒鉛、土状黒鉛など）、人工黒鉛、カーボンブラック、アセチレンブラック、ケッチェンブラック、炭素繊維や金属粉（銅、ニッケル、アルミニウム、銀（特開昭63-148554号）など）、金属繊維あるいはポリフェニレン誘導体（特開昭59-20971号）などの導電性材料を1種又はこれらの混合物として含ませることができる。黒鉛とアセチレンブラックの併用が特に好ましい。その添加量は、1～50質量%が好ましく、特に2～30質量%が好ましい。カーボンや黒鉛では、2～15質量%が特に好ましい。

【0139】本発明では電解液を保持するための結着剤を用いることができる。結着剤の例としては、多糖類、熱可塑性樹脂及びゴム弾性を有するポリマーなどが

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挙げられる。好ましい結着剤としては、でんぷん、カルボキシメチルセルロース、セルロース、ジアセチルセルロース、メチルセルロース、ヒドロキシエチルセルロース、ヒドロキシプロピルセルロース、アルギン酸Na、ポリアクリル酸、ポリアクリル酸Na、ポリビニルフェノール、ポリビニルメチルエーテル、ポリビニルアルコール、ポリビニルピロリドン、ポリアクリロニトリル、ポリアクリルアミド、ポリヒドロキシ(メタ)アクリレート、スチレン-マレイン酸共重合体等の水溶性ポリマー、ポリビニルクロリド、ポリテトラフルオロエチレン、ポリフッ化ビニリデン、テトラフルオロエチレン-ヘキサフルオロプロピレン共重合体、ビニリデンフロライド-テトラフルオロエチレン-ヘキサフルオロプロピレン共重合体、ポリエチレン、ポリプロピレン、エチレン-プロピレン-ジエンターポリマー(EPDM)、スルホン化EPDM、ポリビニルアセタール樹脂、メチルメタアクリレート、2-エチルヘキシルアクリレート等の(メタ)アクリル酸エステルを含有する(メタ)アクリル酸エステル共重合体、(メタ)アクリル酸エステル-アクリロニトリル共重合体、ビニルアセテート等のビニルエステルを含有するポリビニルエステル共重合体、スチレン-ブタジエン共重合体、アクリロニトリル-ブタジエン共重合体、ポリブタジエン、ネオプレンゴム、フッ素ゴム、ポリエチレンオキッド、ポリエステルポリウレタン樹脂、ポリエーテルポリウレタン樹脂、ポリカーボネートポリウレタン樹脂、ポリエステル樹脂、フェノール樹脂、エポキシ樹脂等のエマルジョン(ラテックス)あるいはサスペンションを挙げることができる。特にポリアクリル酸エステル系のラテックス、カルボキシメチルセルロース、ポリテトラフルオロエチレン、ポリフッ化ビニリデンが好ましく挙げられる。これらの結着剤は単独又は混合して用いることができる。結着剤の添加量が少ないと電極合剤の保持力・凝集力が弱い。多すぎると電極体積が増加し電極単位体積あるいは単位質量あたりの容量が減少する。このような理由で結着剤の添加量は1~30質量%が好ましく、特に2~10質量%が好ましい。

【0140】前記フィラーは、構成された電池において、化学変化を起こさない繊維状材料であれば何でも用いることができる。通常、ポリプロピレン、ポリエチレンなどのオレフィン系ポリマー、ガラス、炭素などの繊維が用いられる。フィラーの添加量は特に限定されないが、0~30質量%が好ましい。

【0141】本発明の電解質組成物は、安全性確保のためにセパレーターと併用して使用することが可能である。安全性確保のため併用されるセパレーターは、80℃以上で上記の閉塞を閉塞して抵抗を上げ、電流を遮断する機能を持つことが必要であり、閉塞温度が90℃以上180℃以下であることが好ましい。

【0142】セパレーターの孔の形状は通常円形や楕円

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形で、大きさは0.05~30μmであり、0.1~20μmが好ましい。さらに延伸法、相分離法で作った場合のように、楕状や不定形の孔であってもよい。これらの隙間の占める比率すなわち気孔率は20~90%であり、35~80%が好ましい。

【0143】これらのセパレーターは、ポリエチレン、ポリプロピレンなどの単一の材料であっても、2種以上の複合化材料であってもよい。特に孔径、気孔率や孔の閉塞温度などを変えた2種以上の微多孔フィルムを積層したものが特に好ましい。

【0144】正・負極の集電体としては、構成された電池において化学変化を起こさない電子伝導体を用いられる。正極の集電体としては、アルミニウム、ステンレス鋼、ニッケル、チタンなどの他に、アルミニウムやステンレス鋼の表面にカーボン、ニッケル、チタンあるいは銀を処理させたものが好ましく、特に好ましいのはアルミニウム、アルミニウム合金である。負極の集電体としては、銅、ステンレス鋼、ニッケル、チタンが好ましく、特に好ましいのは銅および銅合金である。

【0145】集電体の形状は、通常フィルムシート状のものが使用されるが、ネット、パンチされたもの、ラステ、多孔質体、発泡体、繊維群の成形体なども用いることができる。厚みは、特に限定されないが、1~500μmである。また、集電体表面は、表面処理により凹凸を付けることも望ましい。

【0146】電池の形状はシート、角、シリンダーなどいずれにも適用できる。正極活物質や負極材料の合剤は、集電体の上に塗布(コート)、乾燥、圧縮されて、主に用いられる。塗布方法としては、例えば、リバースロール法、ダイレクトロール法、ブレード法、ナイフ法、エクストルージョン法、カーテン法、グラビア法、バー法、ディップ法及びスキーズ法を挙げることができる。その中でもブレード法、ナイフ法及びエクストルージョン法が好ましい。塗布は、0.1~100m/分の速度で実施されることが好ましい。この際、合剤の溶液物性、乾燥性に合わせて、上記塗布方法を決定することにより、良好な塗布層の表面状態を得ることができる。塗布は、片面ずつ逐時でも両面同時でもよい。

【0147】また、塗布は連続でも間欠でもストライプでもよい。その塗布層の厚み、長さや巾は、電池の形状や大きさにより決められるが、片面の塗布層の厚みは、ドライ後の圧縮された状態で、1~2000μmが好ましい。

【0148】電極シート塗布物の乾燥及び脱水分方法は、熱風、真空、赤外線、遠赤外線、電子線及び低湿風を単独あるいは組み合わせた方法を用いることができる。乾燥温度は80~350℃の範囲が好ましく、特に100~250℃の範囲が好ましい。含水量は、電池全体で2000ppm以下が好ましく、正極合剤、負極合剤や電解質ではそれぞれ500ppm以下にすることが好まし

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い、シートのプレス法は、一般に採用されている方法を用いることができるが、特にカレンダープレス法が好ましい。プレス圧は、特に限定されないが、0.2〜3t/cm²が好ましい。カレンダープレス法のプレス速度は0.1〜50m/分が好ましく、プレス温度は室温〜200℃が好ましい。正極シートに対する負極シート幅の比は、0.9〜1.1が好ましく、0.95〜1.0が特に好ましい。正極活物質と負極材料の含有量比は、化合物種類や合剤処方により異なる。

【0149】正・負の電極シートをセパレーターを介して重ね合わせた後、そのままシート状電池に加工したり、折りまげた後角形缶に挿入し、缶とシートを電気的に接続した後、本発明の電解質組成物を注入し、封口板を用いて角形電池を形成する。また、正・負の電極シートをセパレーターを介して重ね合わせ巻いた後、シリンダー状缶に挿入し、缶とシートを電気的に接続した後、本発明の電解質組成物を注入し、封口板を用いてシリンダー電池を形成する。この時、安全弁を封口板として用いることができる。安全弁の他、従来から知られている種々の安全素子を備えつけてもよい。例えば、過電流防止素子として、ヒューズ、バイメタル、PTC素子などが用いられる。

【0150】また、安全弁のほかに電池缶の内圧上昇の対策として、電池缶に切込を入れる方法、ガasket亀裂方法、封口板亀裂方法あるいはリード板との切断方法を利用することができる。また、充電器に過充電や過放電対策を組み込んだ保護回路を具備させるか、あるいは独立に接続させてもよい。

【0151】また、過充電対策として、電池内圧の上昇により電流を遮断する方式を具備することができる。このとき、内圧を上げる化合物を合剤あるいは電解質に含ませることができる。内圧を上げるために用いられる化合物の例としては、Li₂CO₃、LiHCO₃、Na₂CO₃、NaHCO₃、CaCO₃、MgCO₃などの炭酸塩などを挙げることができる。

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*【0152】缶やリード板は、電気伝導性をもつ金属や合金を用いることができる。例えば、鉄、ニッケル、チタン、クロム、モリブデン、銅、アルミニウムなどの金属あるいはそれらの合金が用いられる。

【0153】キャップ、缶、シート、リード板の溶接法は、公知の方法（例えば、直流又は交流の電気溶接、レーザー溶接、超音波溶接）を用いることができる。封口用シール剤は、アスファルトなどの従来から知られている化合物や混合物を用いることができる。

【0154】本発明の非水二次電池の用途は、特に限定されないが、例えば、電子機器に搭載する場合、ノートパソコン、ペン入力パソコン、モバイルパソコン、電子ブックプレーヤー、携帯電話、コードレスフォン子機、ページャー、ハンディターミナル、携帯ファックス、携帯コピー、携帯プリンター、ヘッドホンステレオ、ビデオムービー、液晶テレビ、ハンディクリーナー、ポータブルCD、ミニディスク、電気シェーバー、トランシーバー、電子手帳、電卓、メモリーカード、携帯テープレコーダー、ラジオ、バックアップ電源、メモリーカードなどが挙げられる。その他民生用として、自動車、電動車両、モーター、照明器具、玩具、ゲーム機器、ロードコンディショナー、時計、ストロボ、カメラ、医療機器（ペースメーカー、補聴器、肩もみ機など）などが挙げられる。更に、各種軍需用、宇宙用として用いることができる。また、太陽電池と組み合わせることもできる。

【0155】

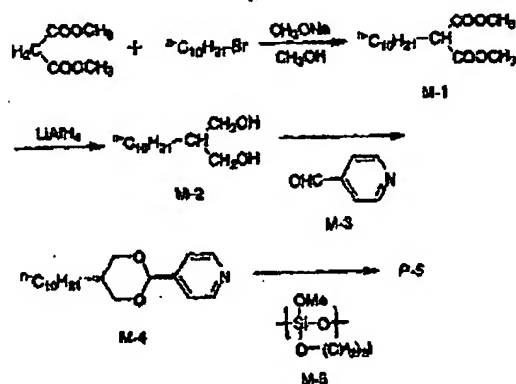
【実施例】以下、本発明を実施例によって具体的に説明する。

ー例示化合物P-5の合成例ー

下記合成スキームにより、例示化合物P-5を合成した。

【0156】

【化18】



【0157】①中間体M-1の合成

マロン酸ジメチル；58.1g（439mmol）をメタノールに溶解し、ナトリウムメトキシのメタノール

28%溶液；88mlを加え、1-ブロモデカン97.2g（439mmol）を1時間かけて滴下した後、8時間還流した。反応混合物を希塩酸に注ぎ中和後、酢酸

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エチルで抽出した。抽出溶液を硫酸マグネシウムで乾燥後、減圧濃縮し、残留物を減圧蒸留し、M-1を41g (399 Pa (3 mmHg) / 82℃の留分) 得た。

【0158】②中間体M-2の合成

リチウムアルミニウムヒドライド (11g, 289 mmol) を150 mlのジエチルエーテルに分散し、室温で攪拌しながら、上記①で得た、M-1 (41g, 170 mmol) をジエチルエーテル (50 ml) に溶解した溶液を2時間かけて滴下した。滴下後、3時間還流した後、反応混合物を、希硫酸/氷にゆっくり注ぎ、溶液を酸性にした後抽出した。抽出液を硫酸マグネシウムで乾燥後、減圧下溶媒を留去し、粗生成物31gの油状物を得た。粗生成物をシリカゲルカラムクロマトにて精製し、M-2、14gを無色の油状物として得た。

【0159】③中間体M-4の合成

上記で得たM-2 (13.85g, 64 mmol) とM-3 (6.86g, 64 mmol) をトルエン (50 ml) に分散し、パラトルエンスルホン酸 (12g) を加え、水を留去しながら5時間加熱還流した。反応混合物を炭酸カリウム (10g) を加えた水 (100 ml) に注ぎ、酢酸エチルで抽出し、抽出液を乾燥後、溶媒を減圧下留去した。残留物をアセトニトリルで再結晶し、目的のM-4を結晶として7g得た。

【0160】④P-5の合成

上記で得たM-4 (5g, 16.4 mmol) とポリマーM-5 (3g) をアセトニトリル (50 ml)、ジメチルアセトアミド (20 ml) に分散し、80℃で10時間反応させた。反応混合物から減圧下、120℃で溶媒を留去し、目的物である液晶性側鎖を有するP-5 (7.5g) を得た。

【0161】(実施例1)

-光電気化学電池-

1-1. 二酸化チタン分散液の調製

内側をテフロン (登録商標) コーティングした内容積200 mlのステンレス製ベッセルに二酸化チタン (日本アエロジル社 Degussa P-25) 15g、水45g、分散剤 (アルドリッチ社製、Triton X-100) 1g、直径0.5 mmのジルコニアビーズ (ニッカトー社製) 30gを入れ、サンドグラインダーミル (アイメックス社製) を用いて1500 rpmにて2時間分散した。分散物からジルコニアビーズをろ過して除いた。この場合の二酸化チタンの平均粒径は2.5 μmであった。このときの粒径はMALVERN社製マスタ

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ーサイザーにて測定したものである。

【0162】1-2. 色素を吸着したTiO₂電極 (電極A) の作製

フッ素をドーブした酸化スズをコーティングした導電性ガラス (旭硝子製TCOガラス-Uを20 mm×20 mmの大きさに切断加工したもの) の導電面側にガラス棒を用いて上記の分散液を塗布した。この導電面側の一部 (端から3 mm) に粘着テープを張ってスペーサーとし、粘着テープが両端に来るようにガラスを並べて一度に8枚ずつ塗布した。塗布後、粘着テープを剥離し、室温で1日間風乾した。次に、このガラスを電気炉 (ヤマト科学製マッフル炉FP-32型) に入れ、450℃にて30分間焼成した。このガラスを取り出し冷却した後、色素R-1のエタノール溶液 (3×10⁻⁴ mol/リットル) に3時間浸漬した。色素の吸着したガラスを4-tert-ブチルピリジンに15分間浸漬した後、エタノールで洗浄し自然乾燥させた。このようにして得られる感光層の厚さは10 μmであり、半導体微粒子の塗布量は20 g/m²とした。なお、導電性ガラスの表面抵抗は約30 Ω/□であった。

【0163】1-3. 光電気化学電池の作製

上述のようにして作製した色素増感されたTiO₂電極基板 (1 cm×1 cm) に、表1に従って調整した前記特定の液晶化合物或いは比較化合物を含む電解質組成物 (E-102~E-113) のアセトニトリル溶液 (アセトニトリルは組成物と同質量) を塗布し、60℃、減圧下で、TiO₂電極に染み込ませながらアセトニトリルを留去した。これらの電極に、同じ大きさの白金蒸着ガラスを重ね合わせ光電気化学電池 (サンプルB-102~113) を得た。また、溶媒を用いた電解液 (表1のE-101) は、上記と同じ色素増感されたTiO₂電極基板 (2 cm×2 cm) に、その電極と同じ大きさの白金蒸着ガラスと重ね合わせた後、両ガラスの隙間に毛細管現象を利用して電解液を染み込ませ、光電気化学電池 (サンプルB-101) を作製した。

【0164】本実施例により、図2に示したとおり、導電性ガラス1 (ガラス2上に導電層3が設けられたもの)、感光層4 (色素を吸着させたTiO₂層)、電解質層5、対極となる白金層6およびガラス7が順に積層された光電気化学電池が作製された。

【0165】

【表1】

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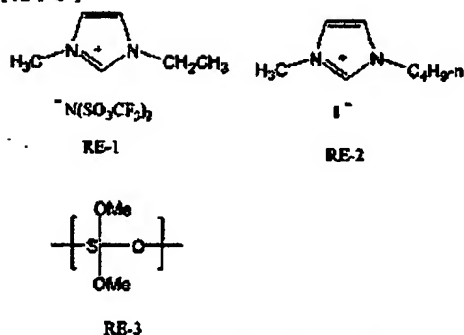
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表1 電解質の組成

電解質	組成 (質量%)	サンプル	備考
E-101	(C ₁₂ H ₁₁ N) ⁺ (48)/BCE(50)/I ₂ (2)	B-101	比較
E-102	(C ₁₂ H ₁₁ N) ⁺ (48)/RE-1(50)/I ₂ (2)	B-102	比較
E-103	RE-2(48)/RE-1(50)/I ₂ (2)	B-103	比較
E-104	(C ₁₂ H ₁₁ N) ⁺ (48)/RE-3(50)/I ₂ (2)	B-104	比較
E-105	P-5 (98) /I ₂ (2)	B-105	本発明
E-106	P-8 (98) /I ₂ (2)	B-106	本発明
E-107	P-11 (98) /I ₂ (2)	B-107	本発明
E-108	P-14 (98) /I ₂ (2)	B-108	本発明
E-109	P-5 (48) /P-6(50)/I ₂ (2)	B-109	本発明
E-110	P-8 (48) /P-9(50)/I ₂ (2)	B-110	本発明
E-111	P-8 (48) /P-10(50)/I ₂ (2)	B-111	本発明
E-112	P-11 (48) /P-12(50)/I ₂ (2)	B-112	本発明
E-113	P-11 (48) /P-13(50)/I ₂ (2)	B-113	本発明

BCE (溶媒): ビスシアノエチルエーテル

【0166】
【化19】

【0167】1-4. 光電変換効率の測定

500Wのキセノンランプ(ウシオ製)の光をAM1.
5フィルター(Oriel社製)およびシャープカット*

表2 光電変換性能

サンプル	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	η (%)	J _{sc} 低下率(%) 80℃-湿度70% 400時間	備考
B-101	11.3	0.60	0.65	4.4	99	比較
B-102	8.1	0.55	0.54	2.4	45	比較
B-103	8.5	0.54	0.56	2.6	23	比較
B-104	8.9	0.57	0.57	3.0	10	比較
B-105	10.4	0.66	0.67	4.3	3	本発明
B-106	10.8	0.66	0.69	4.3	4	本発明
B-107	10.5	0.67	0.68	4.5	3	本発明
B-108	10.6	0.67	0.68	4.6	5	本発明
B-109	11	0.62	0.64	4.3	6	本発明
B-110	11	0.63	0.65	4.5	6	本発明
B-111	11.1	0.63	0.65	4.4	5	本発明
B-112	10.7	0.65	0.64	4.5	5	本発明
B-113	10.5	0.65	0.64	4.3	4	本発明

J_{sc}: 短絡電流密度, V_{oc}: 開放電圧, FF: 形状因子, η: 変換効率

【0170】上記結果から、溶媒を電解液として用いた光電気化学電池(B-101)は、溶媒が揮発するため耐久性が非常に悪いことがわかる。また、比較化合物の溶融塩RE-1、RE-2を用いた電池(B-102、B-103)、及び液晶性置換基を有しないポリシロキサンRE-3を用いた電池(B-104)は経時での劣化は小さいが光電変換性能が十分ではないことがわかる。それらに対して、前記特定の液晶化合物を含む電解質組成物を用いた光電気化学電池は、短絡電流密度、変

*フィルター(KenkoL-41)を通すことにより紫外線を含まない模擬太陽光を発生させ、この光の強度を100mW/cm²に調整した。

【0168】前述の光電気化学電池の導電性ガラスと白金蒸着ガラスにそれぞれ、ワニ口クリップを接続し、70℃にて、模擬太陽光を照射し、発生した電気を電流電圧測定装置(ケースレーSMU238型)にて測定した。これにより求められた光電気化学電池の開放電圧(V_{oc})、短絡電流密度(J_{sc})、形状因子(FF) [=最大出力/(開放電圧×短絡電流)]、および変換効率(η)と恒温恒湿(60℃、70%R.H.)下で、400時間経時した後の短絡電流密度の低下率を一括して表2に記載した。

【0169】

【表2】

換効率等の初期性能、耐久性ともに優れている。このような効果はいずれの色素を用いた場合にも見られた。

【0171】(実施例2)

ーリチウム2次電池ー

2-1. 正極シートの作製

正極活性物質として、LiCoO₂を43重量部、薄片状黒鉛2重量部、アセチレンブラック2重量部、さらに結着剤としてポリアクリロニトリル3重量部を加え、アクリロニトリル100重量部を媒体として混練して得られ

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たスラリーを厚さ20 μ mのアルミニウム箔にエクストルージョン式塗布機を使って塗設し、乾燥後カレンダープレス機により圧縮成形した後、端部にアルミニウム製のリード板を溶接し、厚さ95 μ m、幅54mm×長さ49mmの正極シートを作製した。

【0172】2-2. 負極シートの作製

負極活性物質としてメソフェースピッチ系炭素材料（ベトカ社）を43重量部、導電剤としてアセチレンブラック2重量部とグラファイト2重量部の割合で混合し、さらに結着剤としてポリアクリロニトリルを3重量部を加え、N-メチルピロリドン100重量部を媒体として混練して負極合剤スラリーを得た。負極合剤スラリーを厚さ10 μ mの銅箔にエクストルージョン式塗布機を使って塗設し、乾燥後カレンダープレス機により圧縮成形して厚さ46 μ m、幅55mm×長さ50mmの負極シートを作製した。負極シートの端部にニッケル製のリード板を溶接した後、露点-40℃以下の乾燥空气中で230℃で1時間熱処理した。熱処理は遠赤外線ヒーターを用いて行った。

【0173】2-3. シート電池の作製

負極シート、正極シートはそれぞれ露点-40℃以下の*

表3 電解質の組成

電解質番号	電解質組成 (質量%)	電池番号	備考
E-201	RE-4(30)/PC(30)/EC(40)	B-201	比較
E-202	RE-4(30)/PE-1(70)	B-202	比較
E-203	RE-4(50)/PG1000	B-203	比較
E-204	LiClO ₄ (30)/PE-3(70)	B-204	比較
E-205	P-17(100)	B-205	本発明
E-206	P-19(100)	B-206	本発明
E-207	P-21(100)	B-207	本発明
E-208	P-22(100)	B-208	本発明
E-209	P-17(50)/P-18(50)	B-209	本発明
E-210	P-19(50)/P-20(50)	B-210	本発明
E-211	RE-3(30)/P-18(70)	B-211	本発明
E-212	RE-3(30)/P-20(70)	B-212	本発明
E-213	LiBF ₄ (30)/P-23(70)	B-213	本発明

RE-4: LiH(SO₄CF₃)₂

PC: プロピレンカーボネート

EC: エチレンカーボネート

PG1000: ポリエチレングリコール (平均分子量1000)

【0176】2-4. 電池性能の評価

上記の方法で作製したシート型電池について、電流密度1.3mA/cm²、充電終止電圧4.2V、放電終止電圧2.6V、の条件で充放電を30回繰り返し、30サイクル目における放電容量を求めた。これを同一処方の5個の電池について調べ、その平均をその電池の容量とした。このようにして各々の電池の容量を求め、サン

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*乾燥空气中で230℃で30分脱水乾燥した。ドライ雰囲気中で、幅54mm×長さ49mmの脱水乾燥済み正極シート、幅60mm×長さ60mmに切断したセパレータ（ポリエチレン多孔フィルム）および不織布を積層し、不織布の上に表3に従って調整した組成の電解質（E-202～213）を同量のアセトニトリルに溶解した液を塗布し、50℃で減圧下、アセトニトリルを除去した。また溶媒を用いた電解液（E-201）は、そのままそのまま不織布に染み込ませた。その上に幅55mm×長さ50mmの脱水乾燥済み負極シートを積層し、ポリエチレン（50 μ m）-ポリエチレンテレフタレート（50 μ m）のラミネートフィルムよりなる外装材を使用し4縁を真空下で熱融着して密閉し、シート型電池（サンプルB-201～213）を作製した。

【0174】本実施例により、図3に示したとおり、負極端子35を備えた負極シート33、高分子固体電解質32、および正極端子34を備えた正極シート31が順に積層されたシート型電池が作製された。

【0175】

20 【表3】

ブルB-201に対する相対容量を求めた。また、それぞれの電池の200サイクル目の放電容量を求め、10サイクル目の放電容量に対する比を計算しサイクル容量として表した。それぞれの値を表4に示した。

【0177】

【表4】

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表4 電池性能

電池番号	相対容量	サイクル容量	備考
B-201	1	0.30	比較
B-202	0.59	0.91	比較
B-203	0.31	0.77	比較
B-204	0.70	0.91	比較
B-205	0.88	0.95	本発明
B-206	0.87	0.95	本発明
B-207	0.85	0.96	本発明
B-208	0.86	0.98	本発明
B-209	0.95	0.95	本発明
B-210	0.94	0.94	本発明
B-211	0.96	0.94	本発明
B-212	0.98	0.93	本発明
B-213	0.96	0.94	本発明

【0178】上記結果より、前記特定の液晶化合物を含む電解質は、容量の大きな低下が見られずにサイクル性を向上させていることがわかる。

【0179】これら実施例より、前記特定の液晶化合物を用いることで、実質的に毎発せず、かつ電荷輸送性能に優れた電解質が得られ、これにより、光電変換特性に優れ、経時での特性劣化が少ない光電気化学電池が得られた。さらに、この電解質は、電池容量を低下させず、しかもサイクル特性の優れたリチウムイオン伝導材料であることがわかる。

【0180】

【発明の効果】以上、本発明によれば、耐久性、イオン導電率に優れた電解質組成物を提供することができ、さらに当該電解質組成物を用いた、耐久性、電気特性（光電変換特性）に優れた電気化学電池、非水二次電池、及び光電気化学電池を提供することができる。

【図面の簡単な説明】

【図1】 本発明の光電変換素子の一例を示す概略構成図である。

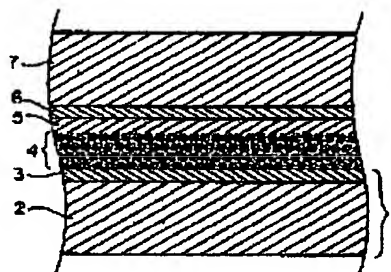
【図2】 実施例2で作製した光電気化学電池の構成を示す断面図である。

【図3】 実施例3で作製したシート型電池の概略図である。

【符号の説明】

- * 1 導電性ガラス
- 2 ガラス
- 3 導電層
- 4 感光層（色素吸着させたTiO₂層）
- 5 電解質層
- 6 白金層
- 7 ガラス
- 10 光電変換素子
- 12 導電層
- 14 下塗り層
- 16 感光層
- 18 電荷輸送層
- 20 対極導電層
- 24 半導体層
- 26 基板
- 28 基板
- s 半導体微粒子
- d 色素
- 1 電荷輸送材料
- 31 正極シート
- 32 高分子固体電解質
- 33 負極シート
- 34 正極端子
- * 35 負極端子

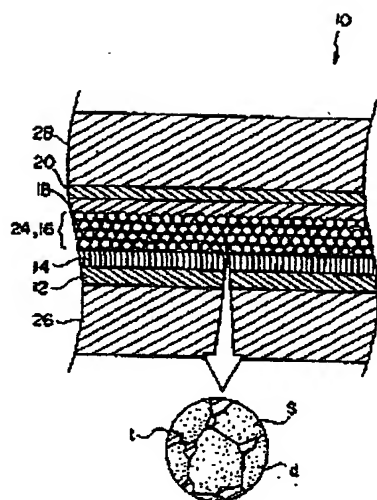
【図2】



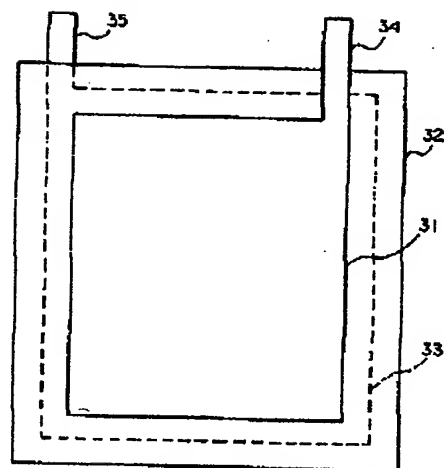
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【図1】



【図3】



フロントページの続き

Fターム(参考) 5F051 AA14 GA02 GA03 GA06
 5G301 CA30 CD01
 5H029 AJ05 AK02 AK03 AL02 AL04
 AL06 AL07 AL08 AM03 AM04
 AM05 AM06 AM07 AM16 DJ09
 EJ04 EJ12
 5H032 AA06 AS16 CC11 CC17 EE16
 EE20

* NOTICES *

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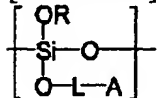
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CLAIMS

[Claim(s)]

[Claim 1] The electrolyte constituent containing the liquid crystal compound which repeats the polysiloxane structure shown by the following general formula (I), and it has as a unit.

[Formula 1]



一般式 (I)

R expresses an alkyl group among [general formula (I), and L expresses single bond or a divalent connection machine. A expresses a mesomorphism substituent. However, a mesomorphism substituent may have an ionicity basis and a mesomorphism substituent contains the counter ion in that case.]

[Claim 2] The electrolyte constituent according to claim 1 characterized by the aforementioned mesomorphism substituent being the salt which consists of an anion part containing a meso gene machine, and a cation part which consists of the opposite cation.

[Claim 3] The electrolyte constituent according to claim 2 with which the aforementioned pair cation is characterized by being alkali-metal ion.

[Claim 4] The electrolyte constituent according to claim 1 characterized by the aforementioned mesomorphism substituent being the salt which consists of a cation part containing a meso gene machine, and an anion part which consists of the opposite anion.

[Claim 5] The electrolyte constituent according to claim 4 characterized by being chosen from the group which the aforementioned pair anion becomes from an iodine anion, a sulfonamide and disulfon imide, N-acyl sulfonamide, a carboxylic acid, a sulfonic acid, alcohol, an activity methylene, and the anion that activity methine dissociated.

[Claim 6] The electrolyte constituent according to claim 1 to 5 characterized by the aforementioned liquid crystal compound being a polymer-liquid-crystal compound obtained by carrying out a polymerization.

[Claim 7] The electrochemical cell characterized by including an electrolyte constituent according to claim 1 to 6.

[Claim 8] The charge transporting bed which contains an electrolyte constituent according to claim 1 to 6 on a conductive base material, the photosensitive layer containing the semiconductor by which sensitization was carried out with coloring matter, and the photoelectrochemical cell characterized by having a counter electrode.

[Claim 9] The non-water rechargeable battery characterized by including an electrolyte constituent according to claim 1 to 6.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the electrolyte constituent containing a liquid crystal compound, the electrochemical cell using electrolyte ***** especially a non-water rechargeable battery, and a photoelectrochemical cell further.

[0002]

[Description of the Prior Art] The electrolyte used for electrochemical cells, such as a non-water rechargeable battery and a coloring matter sensitization solar battery, is a medium which has the function (it is called ionic conduction) to convey the ion to inter-electrode, including the carrier ion according to the purpose. For example, in the lithium secondary battery which is the representation of a non-water rechargeable battery, transportation of a lithium ion does the influence for the performance of an electrochemical cell with the big conductivity of iodine ion and iodine trimer ion in a coloring matter sensitization solar battery. In these cells, generally, although the solvent system with high ion conductivity was used abundantly as an electrolyte, there was a problem of an exhaustion of the solvent at the time of including in a cell and leakage reducing the endurance of a cell. Moreover, in order to seal a solution in a lithium secondary battery and to have to use a metal vessel, it was difficult for cell mass to become heavy and to also give flexibility to a cell configuration. In order to conquer the fault of such a solution system electrolyte, various electrolytes are proposed in recent years. The so-called gel electrolyte (JP,61-23945,B public relations, JP,61-23947,B public relations) which made the solution electrolyte permeate a polymer matrix has not inhibited volatilization of a solvent completely, although the fall of the ionic conductivity to a solution system electrolyte does not drop a cell performance small. Moreover, although the polymer electrolyte (-2184 or K Murata, Electrochimica Acta, Vol.40, No.13-14, and p2177 1995) which dissolved the salt in polymer, such as a polyethylene oxide, is expected as what solves the problem of a solution system electrolyte, ionic conductivity's is not yet enough. On the other hand, although an opposite anion is room temperature fused salt with imidazolium salts and pyridinium salts liquefied at a room temperature, such as BF₄⁻ and 2 (CF₃SO₂)N⁻, and it is proposed as an electrolyte for lithium ion batteries, an electrolytic mechanical strength and ion conductivity conflict, and when own viscosity of fused salt was raised, or it is the means of making polymer contain etc. and a mechanical strength is strengthened, the fall of ionic conductivity is seen. Furthermore, ion conductivity temperature dependence was large and the above electrolytes of especially the ion conductivity in low temperature were inadequate.

[0003] By the way, although compound solar batteries, such as a single-crystal-silicon solar battery, a polycrystal silicon solar cell, an amorphous-silicon solar cell, a cadmium telluride, and selenium-ized indium copper, are set as the object of utilization or research and development, the photovoltaics which transform a light energy into electrical energy need to conquer troubles, such as reservation of a manufacturing cost and raw material, and the length of an energy pay back time, when making it spread. On the other hand, although many solar batteries using the organic material which pointed to large-area-izing or low-pricing were also proposed until now, the conversion efficiency was low and there was a problem that endurance was also bad.

[0004] In such a situation, the technology of a photoelectrochemical cell using the optoelectric transducer (it abbreviates to a coloring matter sensitization optoelectric transducer henceforth) using http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web CGI_ejje

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the oxide semiconductor by which sensitization was carried out to Nature (the 353rd volume, the 737-740th page, 1991), U.S. JP,4927721,B, etc. with coloring matter, and this was indicated. This cell consists of the optoelectric transducer, charge transfer layer, and counter electrode which function as a negative electrode. An optoelectric transducer consists of a conductive base material and a photosensitive layer, and a photosensitive layer contains the semiconductor with which coloring matter stuck to the front face. A charge transfer layer consists of an oxidation reduction object, and bears charge transportation between a negative electrode and a counter electrode (positive electrode). In the photoelectrochemical cell proposed by the above-mentioned patent, the solution (electrolytic solution) which uses salts, such as potassium iodide, as an electrolyte as a charge transfer layer was used. This method was cheap and it was a problem for a photoelectric conversion efficiency not to fall remarkably by evapotranspiration of the electrolytic solution and exhaustion, if it is used over a long period of time, although it is promising, or to stop functioning as a cell in that a comparatively high energy conversion efficiency (photoelectric conversion efficiency) is obtained.

[0005] The method of using as an electrolyte the imidazolium salt which is a low melting point compound as the exhaustion prevention method of the electrolytic solution at WO 95/No. 18456 is indicated to this problem. Since according to this method water and the organic solvent which were used as an electrolytic solvent were unnecessary or little and ended conventionally, although the improvement of endurance was found, still, when endurance is inadequate and the imidazolium salt was made into high concentration, while viscosity became high, charge transportation ability fell, and there was a problem that a photoelectric conversion efficiency became low. Furthermore, there is the method of using a thoria ZORIUMU salt as an electrolyte, and the same problem as an imidazolium salt arises also in this method.

[0006] As mentioned above, it is a very difficult technical problem that it is compatible in a mechanical strength and ion conductivity as an electrolyte of electrochemical cells, such as a lithium ion rechargeable battery and a solar battery.

[0007] As one method of solving these, making an electrolyte constituent contain a mesomorphism compound is proposed. The part which has the coordination ability to ion, such as an alkyleneoxy machine, as these examples, the compound (JP,11-86629,A) which has a meso gene machine, the compound (JP,4-323260,A) with which the meso gene machine was introduced into the polyethylene-oxide chain, the compound (JP,11-116792,A) which has a mesomorphism part in the side chain of a polyethylene oxide, the compound (JP,6-19923,B) with which the meso gene machine was introduced into the side chain of a polysiloxane through the oligo oxyethylene spacer are shown. These consist of a motile flexible high part which dissolves an electrolyte salt and conducts ion by carrying out complexing to a cation, and an upright part (meso gene machine) for carrying out molecular association, in order to maintain a mechanical strength.

[0008] By the way, in order for an electrolyte to function efficiently in an electrochemical cell from Shigehara's and others latest research (Journal of Power Source, 92 volumes, 120 - 123 pages, 2001), it turns out besides ionic conductivity being high that it conducts more nearly alternatively [carrier ion], i.e., it is a performance overlay important point that the carrier ion transference number is high. For example, in a lithium ion battery, it is desirable for the iodine anion transference number to be high in the coloring matter sensitization solar battery from which the lithium ion transference number's being high and an iodine anion serve as a carrier. In the mesomorphism compound mentioned above, the strong basis of cations, such as a polyalkylene oxide, and an interaction restricted the cation, and has caused decline in the cation transference number. Moreover, since molecular-motion nature falls, the improvement in the ionic conductivity itself is not expectable with complexing with a cation, either.

[0009] The oligo oxyethylene part which the polysiloxane by which alkylation was carried out to the electrolyte constituent which introduced the meso gene machine into the side chain of the polysiloxane which shows **** and is indicated by Japanese Patent Publication No. [like] No. 19923 [six to] on the other hand is illustrated, and, as for this electrolyte constituent, restricts a cation strongly serves as a medium of ionic conduction, and is the expectable [the high cation transference number] present condition.

[0010]

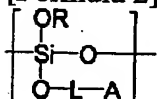
[Problem(s) to be Solved by the Invention] this invention solves many problems in the aforementioned former, and makes it a technical problem to attain the following purposes. That is, the first purpose of this invention is offering the electrolyte constituent excellent in endurance and ion conductivity. Furthermore, the second purpose of this invention is offering the electrochemical cell excellent in endurance and the electrical property (photoelectric transfer characteristic) which used the electrolyte constituent concerned, a non-water rechargeable battery, and a photoelectrochemical cell.

[0011]

[Means for Solving the Problem] The above-mentioned technical problem is solved by the following means. That is, this invention is an electrolyte constituent containing the liquid crystal compound which repeats the polysiloxane structure shown by the <1> following general formula (I), and it has as a unit.

[0012]

[Formula 2]



一般式 (I)

[0013] R expresses an alkyl group among [general formula (I), and L expresses single bond or a divalent connection machine. A expresses a mesomorphism substituent. However, a mesomorphism substituent may have an ionicity basis and a mesomorphism substituent contains the counter ion in that case.]

[0014] The electrolyte constituent of the aforementioned <1> publication characterized by the mesomorphism substituent which A in the <2> aforementioned general formula (I) expresses being the salt which consists of an anion part containing a meso gene machine, and a cation part which consists of the opposite cation.

An electrolyte constituent given in the above <2> whose <3> aforementioned pairs cation is characterized by being alkali-metal ion.

The electrolyte constituent of the aforementioned <1> publication characterized by the mesomorphism substituent which A in the <4> aforementioned general formula (I) expresses being the salt which consists of a cation part containing a meso gene machine, and an anion part which consists of the opposite anion.

An electrolyte constituent given in the above <4> characterized by being chosen from the group which the <5> aforementioned pairs anion becomes from an iodine anion, a sulfonamide and disulfon imide, N-acyl sulfonamide, a carboxylic acid, a sulfonic acid, alcohol, an activity methylene, and the anion that activity methine dissociated.

The electrolyte constituent given [aforementioned] in <1>- <5> characterized by the <6> aforementioned liquid crystal compound being a polymer-liquid-crystal compound obtained by carrying out a polymerization.

[0015] The electrochemical cell characterized by including the electrolyte constituent of a publication in either of <7> aforementioned <1>- <6>.

The charge transporting bed containing an electrolyte constituent given in either of aforementioned <1>- <6> on <8> conductivity base material, the photosensitive layer containing the semiconductor by which sensitization was carried out with coloring matter, and the photoelectrochemical cell characterized by having a counter electrode.

The non-water rechargeable battery characterized by including the electrolyte constituent of a publication in either of <9> aforementioned <1>- <6>.

[0016]

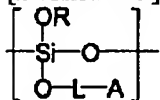
[Embodiments of the Invention] Hereafter, this invention is explained in detail. The electrolyte constituent of this invention comes to contain the liquid crystal compound which repeats the polysiloxane structure shown by the following general formula (I), and it has as a unit.

[0017] As shown in the following general formula (I), this specific liquid crystal compound repeats

the polysiloxane structure by which alkoxy substitution was carried out, and has it as a unit. This polysiloxane structure by which alkoxy substitution was carried out has high maneuverability, and since it can dissolve an electrolyte salt, without restricting a cation strongly, it can realize the cation transference number and ion conductivity higher than an oxyethylene machine. Thus, the polysiloxane structure by which alkoxy substitution was carried out serves as a medium which dissolves an electrolyte salt according to the principal chain, and conducts ion, it is one side, and the part with the upright side chain (mesomorphism substituent) brings about the macroscopic mechanical strength of an electrolyte constituent, without carrying out molecular association, and an ionic conduction medium's forming the structure base material which carried out phase separation micro, and reducing the maneuverability of an ionic conduction medium by mesomorphism. For this reason, the electrolyte constituent of this invention containing a specific liquid crystal compound is excellent in endurance and charge transportability ability.

[0018]

[Formula 3]



一般式 (I)

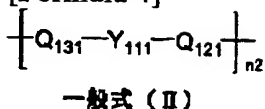
[0019] Carbon atomic numbers (henceforth, more than C) are 1-24 preferably. the inside of a general formula (I), and R -- alkyl group [-- You may be branched-chain, even if it is 1-10 and is a straight chain-like. more -- being desirable (more than C) -- For example, a methyl, ethyl, a propyl, butyl, i-propyl, i-butyl, Pentyl, hexyl, octyl, 2-ethylhexyl, t-octyl, desyl, dodecyl, tetradecyl, 2-hexyl desyl, hexadecyl, octadecyl, cyclohexyl methyl, and octyl cyclohexyl] is expressed. Furthermore, R may have the substituent. as a desirable substituent Carbon atomic numbers (henceforth, more than C) are 1-24 preferably. alkyl group [which may be replaced -- You may be branched-chain, even if it is 1-10 and is a straight chain-like. more -- being desirable (more than C) -- For example, a methyl, ethyl, a propyl, butyl, i-propyl, i-butyl, A pentyl, a hexyl, an octyl, 2-ethylhexyl, t-octyl, A desyl, a dodecyl, tetradecyl, 2-hexyl desyl, hexadecyl, Octadecyl, cyclohexyl methyl, and octyl cyclohexyl], the aryl group (desirable -- more than C [6-24], for example, a phenyl, --) which may be condensing the ring even if it has replaced 4-methylphenyl, 3-cyano phenyl, 2-chlorophenyl, 2-naphthyl, the heterocycle machine that may be condensing the ring even if it has replaced (the nitrogen in a ring may form 4 class at the time of a nitrogen-containing heterocycle machine.) Preferably More than C [2-24], for example, 4-pyridyl, 2-pyridyl, 1-octyl pyridinium-4-IRU, 2-pyrimidyl, 2-imidazolyl, 2-thiazolyl, and alkoxy-group [-- desirable -- more than C [1-24], for example, a methoxy, -- Ethoxy ** butoxy, octyloxy, methoxyethoxy one, methoxy PENTA (ethyloxy), acryloyl oxyethoxy and pentafluoro propoxy] and an acyloxy machine (desirable -- more than C [1-24], for example, acetyloxy, --) benzoyloxy one and an alkoxy carbonyl group (desirable -- more than C [2-24], for example, a methoxycarbonyl, --) Ethoxycarbonyl, a cyano group, a fluoro machine, an alkoxy carbonyl group, a cyano group, and polymerization nature machines (preferably a vinyl group, an acryloyl machine, a methacryloyl machine, a styryl machine, a cinnamic acid residue, etc.) are mentioned.

[0020] L expresses single bond or a divalent connection machine among a general formula (I). As an example of a divalent connection machine, -(CH₂)_n- (n shows the integer of 1-15 here), -CH₂CH₂(OCH₂CH₂)_N- (N Shows Integer of 1-10 Here), -CH=CH-, -CH=N-, -N=N-, -N(O)=N-, -COO-, -COS-, CONH-, -COCH₂-, -CH₂NH-, -CO-, -CH=CH-COO-, -CH=CH-CO-, -(C**C)- (N Shows Integer of 1-3 Here), Such Combination, Etc. are Desirable. -(CH₂)_n- (n shows the integer of 3-10 here), -CH₂CH₂(OCH₂CH₂)_n- (n shows the integer of 2-8 here), and such combination are still more desirable.

[0021] Although a mesomorphism substituent is expressed, a meso gene machine is mentioned as a mesomorphism substituent, for example, the inside of a general formula (I) and A are "Flussige Kristalle in Tabellen II" and Dietrich. Demus and HorstZaschke and the thing of which the 7-18 (1984). publication is done are mentioned. Especially, what is expressed with the following general formula (II) is desirable.

[0022]

[Formula 4]



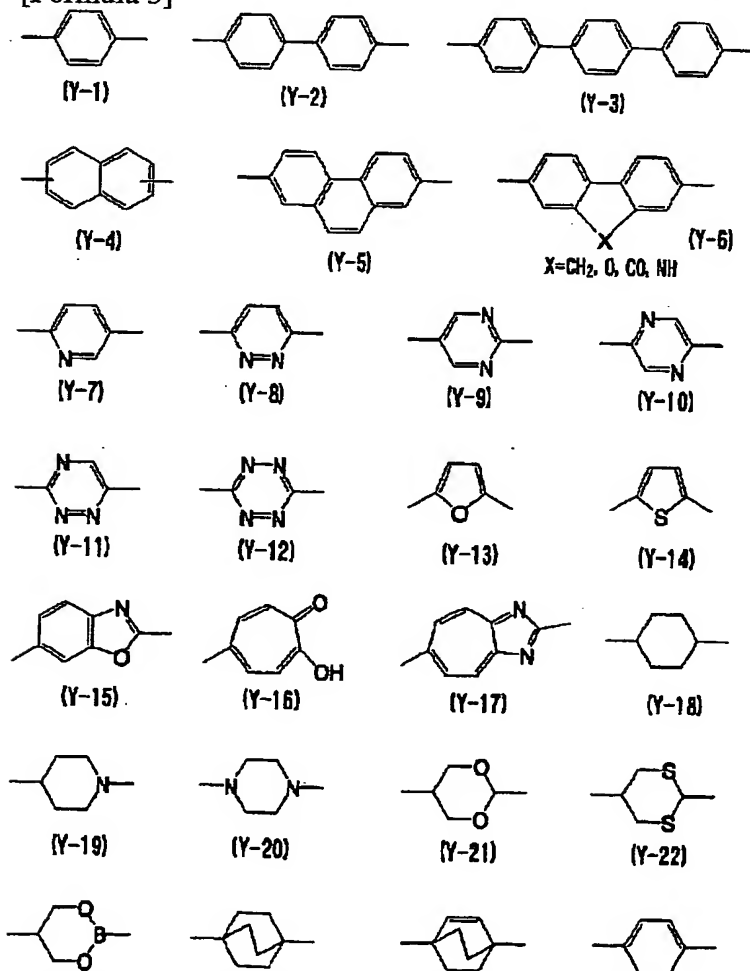
[0023] Y111 expresses the condensed-ring substituent which consists of a divalent 4 or 7 member ring substituent or them among a general formula (II). Q121 and Q131 express a divalent connection machine or divalent single bond, respectively, n2 expresses 1, 2, or 3, and when n2 is 2 or 3, even if two or more Y111, Q121, and Q131 are the same respectively, they may differ.

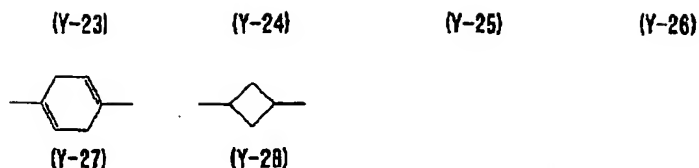
[0024] Q121 and Q131 express a divalent connection machine or divalent single bond among a general formula (II), respectively. As an example of a divalent connection machine, -CH=CH-, -CH=N-, -N=N-, -N(O)=N-, -COO-, -COS-, -CONH-, -COCH2-, -CH2CH2-, -OCH2-, -CH2NH-, -CH2-, -CO-, -O-, -S-, -NH-, -(CH2)1-3-, -CH=CH-COO-, -CH=CH-CO-, -(C**C)1-3-, such combination, etc. are desirable, and -CH2-, -CO-, -O-, -CH=CH-, -CH=N-, -N=N-, and such combination are still more desirable. Moreover, a hydrogen atom may be replaced in these. As for Q121 and Q131, it is desirable that it is especially single bond.

[0025] The inside of a general formula (II), 4, 5, 6 or 7 member ring substituent divalent in Y111, The condensed-ring substituent which consists of them is expressed, and it is still more desirable that they are the saturation of 6 member ring aromatic machine, 4, or 6 member ring or an unsaturation aliphatic machine, 5, 6 member ring heterocycle machines, or those condensed rings. or as these examples Although the following formula (Y-1) - (Y-27) a substituent are mentioned, it is not limited to these. Moreover, you may be such combination. The still more desirable things in these substituents are (Y-1), (Y-2), (Y-18), (Y-19), (Y-21), and (Y-22), and especially desirable things are (Y-1), (Y-2), and (Y-21).

[0026]

[Formula 5]





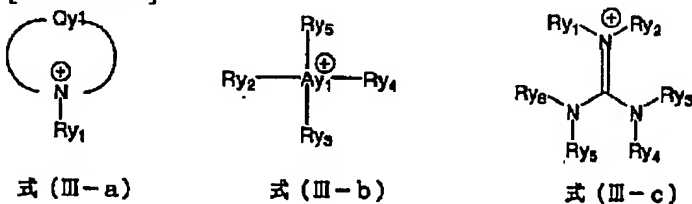
[0027] A mesomorphism substituent may have an ionicity basis and a mesomorphism substituent comes to form the so-called anion part and the so-called cation part, and the salt structure constituted in that case including the counter ion. In case a specific liquid crystal compound adjusts an electrolyte, it can make carrier ion the counter ion of the liquid crystal compound which is ionicity, because this liquid crystal substituent has salt structure. For this reason, since there is no need of adding carrier ion in the form of a salt, separately and mobile ion other than carrier ion is not contained, the transference number of carrier ion can be raised. In this case, the basis which gives mesomorphism as a mesomorphism substituent, for example, a meso gene machine, is contained at least in one side of an anion part and a cation part. The basis which gives mesomorphism may not be included or organic ion (an organic anion, organic cation) or inorganic ion (an inorganic anion, inorganic cation) is sufficient as the anion part or cation part of the direction which has not been directly connected with L in a general formula (I).

[0028] The salt which consists of a salt which consists of an anion part containing a meso gene machine and a cation part which consists of the opposite cation as suitable concrete composition of a mesomorphism substituent or a cation part containing a meso gene machine, and an anion part which consists of the opposite anion is mentioned. It comes to connect either these anions part and a cation part with L in a general formula (I).

[0029] When a meso gene machine is included in a cation part, structure desirable as the cation part (substituent with a positive charge) is a general formula (III-a) or (III-b) (III-c) structure expressed. As for a meso gene machine, at this time, it is desirable to be contained as a substituent of Ry1-Ry5 in general formula (III-a) - (III-c), or Qy1. Moreover, it is desirable to be contained as the atomic groups Ry1-Ry5 which consist of a repeat unit shown by the aforementioned general formula (I), or a substituent of Qy1.

[0030]

[Formula 6]



[0031] Qy1 of a general formula (III-a) expresses the atomic group which can form the aromatic cation of 5 or 6 member ring with a nitrogen atom, and Ry1 expresses the alkenyl machine which is not replaced [the alkyl group which is not replaced / substitution or /, a polymerization nature machine, substitution, or].

[0032] Ay1 of a general formula (III-b) expresses a nitrogen atom or the Lynn atom, and Ry2, Ry3, Ry4, and Ry5 express respectively the alkenyl machine which is not replaced [the alkyl group which is not replaced / substitution or /, a polymerization nature machine, substitution, or] independently. However, Ry2, Ry3, Ry4, and Ry5 are not aryl groups simultaneous [three or more]. Moreover, two or more of Ry2, Ry3, Ry4, and Ry5 may form the un-aromatic ring which connects mutually and contains Ay1.

[0033] Respectively, independently, Ry1, Ry2, Ry3, Ry4, Ry5, and Ry6 of a general formula (III-c) may express the alkenyl machine which is not replaced [the alkyl group which is not replaced / substitution or /, a polymerization nature machine substitution, or], among those two or more may connect them mutually, and they may form a ring structure.

[0034] A general formula (III-a), (III-b), and (III-c) the cation expressed may form a polymer through Qy1, or Ry1-Ry6.

[0035] The composition atom of the atomic group Qy1 which can form the cation of aromatic series 5 or 6 member rings with nitrogen is preferably chosen from carbon, hydrogen, nitrogen, oxygen, and sulfur among a general formula (III-a).

[0036] As 6 member rings completed by Qy1, it is a pyridine, a pyrimidine, a pyridazine, a pyrazine, and triazine preferably, and is a pyridine more preferably.

[0037] As a aromatic-series 5 member ring completed by Qy1, it is an oxazole, a thiazole, an imidazole, a pyrazole, an isoxazole, thiadiazole, an OKISA diazole, and a triazole, and they are an oxazole, a thiazole, and an imidazole more preferably. An oxazole and an imidazole are especially desirable.

[0038] A general formula (III-a), and (III-b) (III-c) inner Ry1-inner Ry6 It is the alkyl group (carbon atomic numbers (henceforth, more than C) are 1-24 preferably) which is not replaced [substitution or] independently respectively. Even if it is a straight chain-like, it may be branched-chain, and you may be a ring type. For example, a methyl, ethyl, a propyl, butyl, i-propyl, a pentyl, A hexyl, an octyl, 2-ethylhexyl, t-octyl, a desyl, A dodecyl, tetradecyl, 2-hexyl desyl, octadecyl, cyclohexyl, cyclopentyl and a polymerization nature machine (desirable -- a vinyl group and an acryloyl machine --) Alkenyl machines which are not replaced [substitution or], such as a methacryloyl machine, a styryl machine, and a cinnamic acid residue (more than are 2-24 in C preferably) Even if it is a straight chain-like, it may be branched-chain, for example, a vinyl and an allyl compound are expressed, the alkyl group of more than C 3-18 or the alkenyl machine of more than C 2-18 is expressed preferably, and the alkyl group of more than C 4-6 is expressed more preferably.

[0039] A general formula (III-a), inner Qy1, and Ry1-Ry6 may have the substituent. as an example of a desirable substituent a halogen atom (F, Cl, Br, I), a cyano group, and an alkoxy group (a methoxy -) Ethoxy ** butoxy, octyloxy, methoxyethoxy one, methoxy PENTA (ethyloxy), Aryloxy machines, such as acryloyl oxyethoxy and pentafluoro propoxy one (phenoxy etc.), alkyl thio machines (a methylthio, ethyl thio, etc.) and an acyl group (an acetyl --) sulfonyl machines (a methane sulfonyl --), such as a propionyl and a benzoyl An acyloxies machine, such as benzenesulphonyl (acetoxo, benzoyloxy, etc.), A sulfonyloxy machine (methane sulfonyloxy, toluenesulfonyloxy, etc.), phosphonyl groups (diethyl phosphonyl etc.) and an amide group (acetyl amino --) carbamoyl groups (N and N-dimethyl carbamoyl --), such as a benzoyl amide alkyl groups (a methyl, ethyl, and a propyl --), such as N-phenylcarbamoyl An isopropyl, a cyclo propyl, butyl, 2-carboxy ethyl, a benzyl, etc., aryl groups (a phenyl, toluyl, etc.) and a heterocycle machine (for example, pyridyl --) Alkenyl machines, such as imidazolyl and furanyl (a vinyl, 1-propenyl, etc.), An alkoxy-group acyloxy machine (acetyloxy, benzoyloxy, etc.), Alkoxy carbonyl groups (a methoxycarbonyl, ethoxycarbonyl, etc.) and polymerization nature machines (preferably a vinyl group, an acryloyl machine, a methacryloyl machine, a styryl machine, a cinnamic acid residue, etc.) are mentioned.

[0040] When a meso gene machine is included in a cation part, as the opposite anion preferably As an inorganic anion, a halogen anion (Cl-, Br-, I-), an iodine trimer anion (I3-), NCS-, BF4-, PF6-, O4Cl-, Ph4B-, AsF6-, SbF6-, and B10Cl10-, It is desirable to be chosen from the group which consists of an anion which a sulfonamide, disulfon imide, N-acyl sulfonamide, a carboxylic acid, a sulfonic acid, alcohol, an activity methylene, and activity methine dissociated as an organic anion. It is chosen from the group which consists of an iodine anion (I-, I3-) and an anion which a sulfonamide, disulfon imide, N-acyl sulfonamide, a carboxylic acid, a sulfonic acid, alcohol, an activity methylene, and activity methine dissociated as an organic anion more preferably. As an iodine anion (I-, I3-) and an organic anion, still more preferably A sulfonic acid, the anion (for example, (CnF2n+1SO2) (CmF2m+1SO2), imido anion expressed with N- (n --)) which disulfo nil imide and N-acyl sulfonamide dissociated m is chosen from the group which consists of six or less positive integer, a fluorosulfonic-acid anion (n is six or less positive integer) expressed with CnF2n+1SO3-, respectively. It is an iodine anion (I-, I3-) especially preferably. This iodine anion is advantageous when using a specific liquid crystal compound as an electrolyte use for solar batteries from which iodine ion serves as a carrier.

[0041] When a meso gene machine is included in an anion part, things desirable as the anion part (substituent with a negative charge) are a sulfonamide, disulfon imide, N-acyl sulfonamide, a carboxylic acid, a sulfonic acid, alcohol, an activity methylene, and the anion in which activity

methine carried out proton dissociation.

[0042] When a meso gene machine is included in an anion part, as the above-mentioned general formula (III-a) and (III-b) (III-c) the cation of the structure expressed, and an inorganic cation, a lithium ion is suitably mentioned as an organic cation preferably as the opposite cation. A lithium ion is suitable also especially in these. This lithium ion is advantageous when using a specific liquid crystal compound as a lithium ion battery or an electrolyte for lithium cells.

[0043] It is desirable that an alkyl group or an alkenyl machine is included as a basis which connects with a mesomorphism substituent (the counter ion is also included when it has an ionicity basis) the organic ion which shows an end group or a meso gene machine, and ionicity. As for the carbon number of these alkyl groups or an alkenyl machine, 6 to 25 is desirable, and 6 to 18 is still more desirable. Moreover, you may have the substituent and what was mentioned above as a substituent in R of a general formula (I) as a desirable substituent is mentioned.

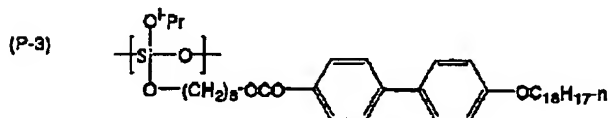
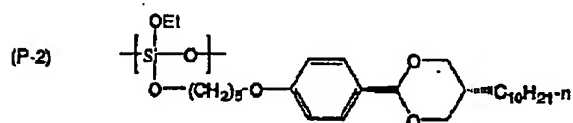
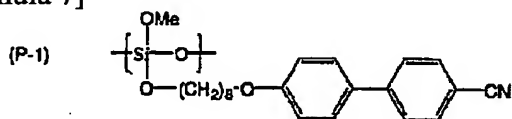
[0044] As a mesomorphism substituent, when using the electrolyte constituent of this invention for a lithium ion battery or a lithium cell use, especially desirable composition is an anion part in which the part connected with L in a general formula (I) contains a meso gene machine, and is the composition that the counter ion used as the cation part is a lithium ion. On the other hand, when using for the solar-battery use from which iodine ion serves as a carrier, it is desirable that it is the composition that the opposite anion which the part connected with L in a general formula (I) is a cation part containing a meso gene machine, and serves as the anion part is iodine ion.

[0045] As a mesomorphism substituent, pKa of the conjugate acid of an anion part is desirable from a viewpoint which raises the dissociation concentration of the ion (for example, a lithium ion, iodine ion, etc.) from which it becomes a carrier in an electrolyte that it is 11 or less, and it is still more desirable that it is seven or less.

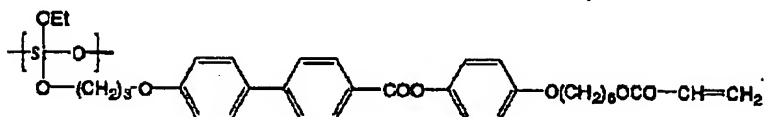
[0046] Although the example P-1 to P-28 of the polysiloxane structure shown by the general formula (I) is shown hereafter, this invention is not necessarily limited to these examples. In addition, let the liquid crystal compound which repeats the structure shown by this example and it has as a unit be the instantiation compound P-1 to P-28.

[0047]

[Formula 7]

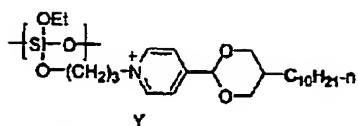


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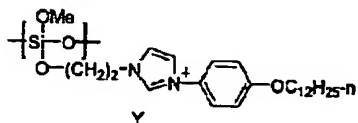


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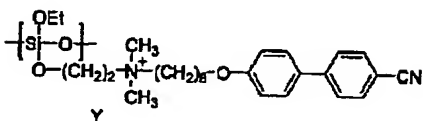
[Formula 8]



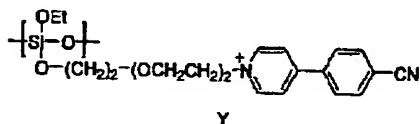
(P-5) Y = I⁻
 (P-6) Y = N(SO₂CF₃)₂⁻
 (P-7) Y = CF₃COO⁻



(P-8) Y = I⁻
 (P-9) Y = N(SO₂CF₃)₂⁻
 (P-10) Y = BF₄⁻



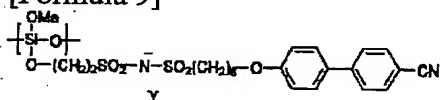
(P-11) Y = I⁻
 (P-12) Y = H₃COOC-C⁻(SO₂CF₃)₂
 (P-13) Y = BF₄⁻



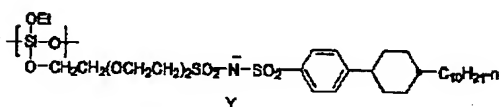
(P-14) Y = I⁻
 (P-15) Y = CF₃CONSO₂CF₃⁻
 (P-16) Y = O(CH₂)₂CH₃

[0049]

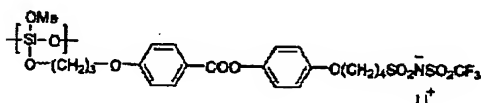
[Formula 9]



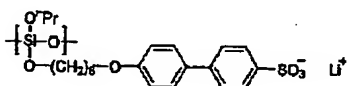
(P-17) Y = Li⁺
 (P-18) Y = $\text{H}_3\text{C}-\text{N}^+ \text{C}_6\text{H}_4 \text{N}^+ \text{CH}_2\text{CH}_3$



(P-19) Y = Li⁺
 (P-20) Y = $\text{H}_3\text{C}-\text{N}^+ \text{C}_6\text{H}_4 \text{N}^+ \text{CH}_2\text{CH}_3$



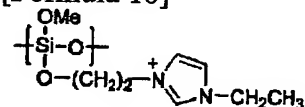
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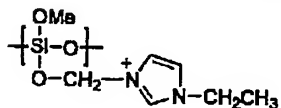
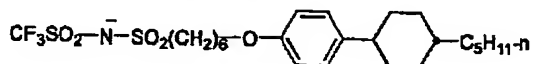
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[0050]

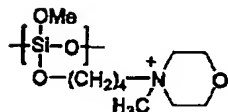
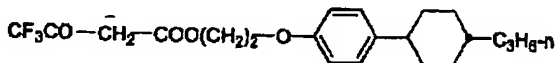
[Formula 10]



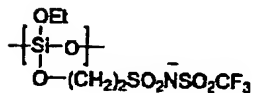
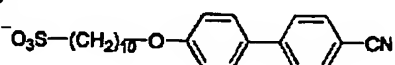
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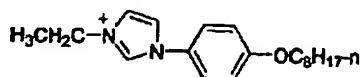
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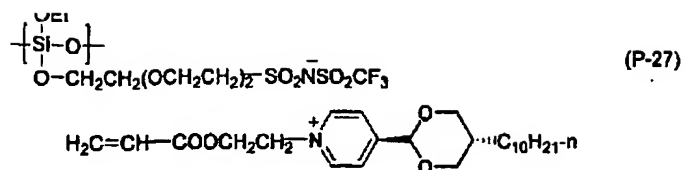


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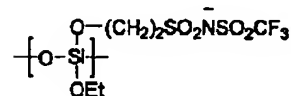
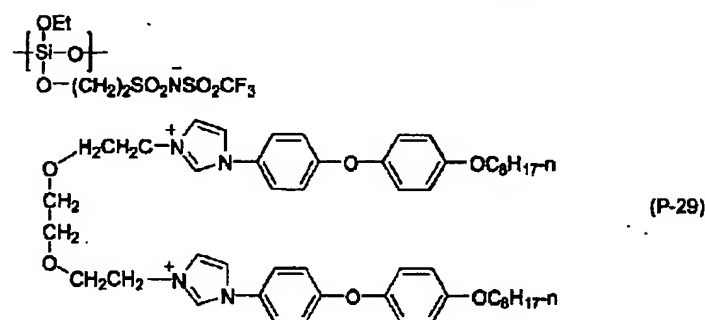
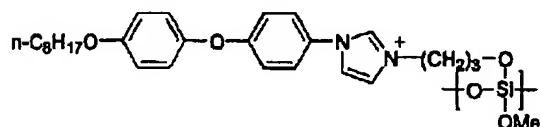
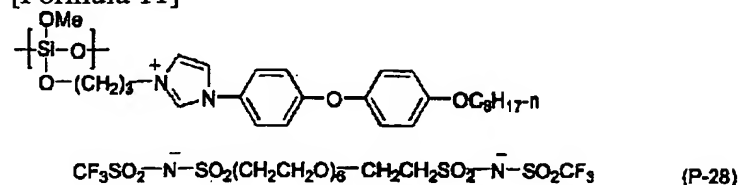
(P-26)





[0051]

[Formula 11]



[0052] A specific liquid crystal compound may be a high molecular compound obtained by having a polymerization nature machine and carrying out the polymerization of them. The radical polymerization method which is a general macromolecule synthesis method indicated by the laboratory procedure (Kagaku-Dojin) of Takayuki Otsu and Kinoshita **** collaboration: macromolecule composition, Takayuki Otsu: lecture polymerization-reaction theory 1 radical polymerization (I), and (Kagaku-Dojin) as a polymerization method which this high molecular compound obtains can be used. The thermal polymerization initiator which there are a thermal polymerization method using a thermal polymerization initiator and the photopolymerizing method using a photopolymerization initiator, and is used preferably For example, 2 and 2'-azobis (isobutyronitrile), 2, and 2'-azobis (2,4-dimethylvaleronitrile), Azo system initiators, such as a dimethyl 2 and 2'-azobis (2-methyl propionate), For the example of the photopolymerization initiator which peroxide system initiators, such as benzoyl peroxide, etc. are contained and is used preferably alpha-carbonyl compound (U.S. JP,2367661,B -- said -- each specification publication of No. 2367670) -- The acyloin ether (U.S. JP,244828,B specification publication), alpha-hydrocarbon substitution aromatic acyloin compound (U.S. JP,2722512,B specification publication), a polynuclear quinone compound (U.S. JP,3046127,B -- said -- each specification publication of No. 2951758) -- The combination of a triaryl imidazole dimer and p-aminophenyl ketone (U.S. JP,35493676,B specification publication), An acridine, a phenazine compound (JP,60-105667,A, the U.S. JP,4239850,B specification publication), and an OKISA diazole compound (U.S. JP,4212970,B specification publication) are contained. The desirable addition of a polymerization initiator is below 20 mass % more than 0.01 mass % to a monomer (salt) total amount, and is below 10 mass % more than 0.1 mass % still more preferably. The desirable molecular weight (number average molecular weight) of the macromolecule obtained by the polymerization is 5,000-1 million, when monomers

(salt) are single organic functions, and it is 10,000-500,000 still more preferably. Moreover, when the case of polyfunctional monomer (salt) or a cross linking agent is used, the polymer of the above-mentioned molecular weight forms the 3-dimensional network structure.

[0053] When using the electrolyte constituent of this invention for the electrolyte of a photoelectrochemical cell, it is desirable to use the electrolyte constituent containing I⁻ and I³⁻ as a charge carrier, and it can add them in the form of arbitrary salts. As an opposite cation of a desirable iodine salt, the above-mentioned general formula (III-a) or (III-b) (III-c) the thing expressed is mentioned. As for an I³⁻-salt, it is common to add iodine (I₂) to the bottom of I-salt existence, and to make it generate in an electrolyte constituent. Added I³⁻ of I₂ and the amount of said generates in that case.

[0054] The concentration of I⁻ in the electrolyte constituent of this invention has desirable 10 - 90 mass %, and its 30 - 70 mass % is still more desirable. It is desirable that all the components of the remainder in that case are specific liquid crystal compounds. In addition, this concentration is the concentration also containing this, when I⁻ is contained as a counter ion in the aforementioned specific liquid crystal compound.

[0055] It is more desirable that it is [0.1-20 mol] %, as for I³⁻, it is desirable that it is [0.1-50 mol / of I⁻] %, and it is / it is still more desirable that it is / 0.5-10 mol / %, and / most desirable that it is / 0.5-5 mol / %. In addition, this rate is this ***** rate, when I³⁻ is contained as a counter ion in the aforementioned specific liquid crystal compound.

[0056] The fused salt which may also contain still more nearly another fused salt in the electrolyte constituent of this invention, and is used preferably The aforementioned general formula (III-a), and (III-b) (III-c) the shown organic cation and arbitrary anions are combined. as an anion Halogenide ion, SCN⁻ (Cl⁻, Br⁻, etc.), BF₄⁻, PF₆⁻, ClO₄⁻, 2 (CF₃SO₂)N⁻, 2 (CF₃CF₂SO₂)N⁻, CH₃SO₃⁻, CF₃SO₃⁻, CF₃COO⁻, Ph₄B⁻, 3(CF₃SO₂) C⁻, etc. are mentioned as a desirable example, and SCN⁻, CF₃SO₃⁻, CF₃COO⁻, 2 (CF₃SO₂)N⁻, and BF₄⁻ are mentioned still more preferably. Moreover, it is desirable that alkali-metal salts, such as LiI, CF₃COOLi, CF₃COONa, LiSCN, and NaSCN, are especially included from a viewpoint on the photoelectrical flow direction. As for the addition of an alkali-metal salt, it is desirable that it is a 0.02 - 2 mass % grade, and its 0.1 - 1 mass % is still more desirable.

[0057] To the electrolyte constituent of this invention, metal iodides, such as LiI, NaI, KI, CsI, and CaI₂, The iodine salt of the 4th class imidazolium compound, the iodine salt of a tetraalkylammonium compound, Metal bromides, such as Br₂, LiBr, NaBr, KBr, CsBr, and CaBr₂, Or the bromine salt of the 4th class ammonium compounds, such as Br₂, a tetrapod alkylammonium star's picture, and a pyridinium star's picture Sulfur compounds, such as metal complexes, such as a ferrocyanic-acid salt-ferricyanic-acid salt and a ferrocene-ferricinium ion, the poly sodium sulfide, and alkyl thiol-alkyl disulfide, viologen coloring matter, a hydroquinone-quinone, etc. are made to contain, and can also be used. When making it contain, as for the amount of these compounds used; it is desirable that it is below 30 mass % of the whole electrolyte constituent.

[0058] the liquid crystal compound and ** of the aforementioned specification in the electrolyte constituent of this invention -- ** -- a solvent can both be preferably used to this compound and a homogeneous amount at the maximum

[0059] As for the solvent used for the electrolyte constituent of this invention, it is desirable for a dielectric constant to be high in improving ionic mobility low, and for viscosity to be the compound which improves effective carrier concentration and can discover the outstanding ion conductivity. As such a solvent, carbonate compounds, such as ethylene carbonate and propylene carbonate, Heterocyclic compounds, such as 3-methyl-2-oxazolidinone, a dioxane, Ether compounds, such as diethylether, ethylene glycol dialkyl ether, The propylene-glycol dialkyl ether, the polyethylene-glycol dialkyl ether, Chain-like ether, such as the polypropylene-glycol dialkyl ether, A methanol, ethanol, ethylene glycol monoalkyl ether, Propylene-glycol monoalkyl ether, polyethylene-glycol monoalkyl ether, Alcohols, such as polypropylene-glycol monoalkyl ether, Ethylene glycol, a propylene glycol, a polyethylene glycol, Polyhydric alcohol, such as a polypropylene glycol and a glycerol, an acetonitrile, Guru taro dinitrile, a methoxy acetonitrile, a propionitrile, Non-proton polar substances, such as ester, such as nitril compounds, such as a benzonitrile, a carboxylate, phosphoric ester, and phosphonate, a dimethyl sulfoxide, and a sulfolane, water, etc. can be used. Also in this, nitril

compounds, such as heterocyclic compounds, such as carbonate compounds, such as ethylene carbonate and propylene carbonate, and 3-methyl-2-oxazolidinone, an acetonitrile, guru taro dinitrile, a methoxy acetonitrile, a propionitrile, and a benzonitrile, and especially ester are desirable. Even if it uses these independently, they may use two or more sorts together.

[0060] As a solvent, the boiling point [in / an ordinary pressure (one atmospheric pressure) / at the viewpoint of the improvement in endurance by volatility-proof] has desirable 200 degrees C or more, its 250 degrees C or more are more desirable, and its 270 degrees C or more are still more desirable.

[0061] in using the electrolyte constituent of this invention for electrochemical cells, such as a lithium ion battery, at least one kind of the compound in an electrolyte constituent contains a lithium element (ion) -- although it comes out and a certain compound is used suitably, as concentration of a lithium element (ion), 5 % of the weight - 100 % of the weight is desirable, and 60 % of the weight is still more desirable from 20 % of the weight

[0062] The electrolyte constituent of this invention can be used for reaction solvents, such as a chemical reaction and metal plating, a CCD (charge-coupled device) camera, various electrochemical cells (the so-called cell), an electrochemistry sensor, a photoelectrical evaporation study sensor, etc. It is more desirable for it to be preferably used for a non-water rechargeable battery (especially lithium secondary battery) and the photoelectrochemical cell using the semiconductor mentioned later, and to be used for a photoelectrochemical cell.

[0063] The electrochemical cell of this invention which used the electrolyte constituent of this invention below for the [electrochemical cell] is explained. Since the electrochemical cell of this invention contains the electrolyte constituent of the aforementioned this invention, it shows the outstanding endurance and outstanding ion conductivity.

[0064] Except the electrochemical cell of this invention containing the electrolyte constituent of the aforementioned this invention as an electrolyte, there is especially no limit and it can take general composition. A general electrochemical cell becomes by composition which sandwiched the electrolyte by the operation pole and the counter electrode, and corresponding to the oxidization (reduction) reaction which occurs by operation best quality, and the reduction (oxidization) reaction which occurs by the counter electrode, when the carrier ion in an electrolyte moves between two poles, it functions. In the case of the photoelectrochemical cell mentioned later, in the case of the electrode (for example, coloring matter sensitization semiconductor electrode) and rechargeable battery from which an operation pole produces electromotive force by optical pumping, the active material which can carry out insertion discharge of the lithium ion in connection with oxidation reduction is used by an operation pole (usually called a positive electrode) and the counter electrode (usually called a negative electrode).

[0065] The photoelectrochemical cell of this invention which used the electrolyte constituent of this invention below for the [photoelectrochemical cell] is explained. The photoelectrochemical cell of this invention has the charge transporting bed which contains an electrolyte constituent on a conductive base material, a photosensitive layer containing the semiconductor by which sensitization was carried out with coloring matter, and a counter electrode, and it constitutes them so that the optoelectric transducer explained to the so-called following may be made to work in an external circuit. The photoelectrochemical cell of this invention shows the outstanding endurance with small degradation of the cell performance in the passage of time while it is excellent in a photo-electric-translation performance, since the aforementioned charge transporting bed contains the electrolyte constituent of this invention.

[0066] [1] An example of an optoelectric transducer applicable to this invention at optoelectric-transducer drawing 1 is shown. A conductive layer 12, an under coat 14, a photosensitive layer 16, the charge transporting bed 18, and the counter electrode conductive layer 20 come to carry out the laminating of the optoelectric transducer 10 one by one. A photosensitive layer 16 turns into the semiconductor layer 24 which carried out sensitization with coloring matter d from the charge transportation material t. The semiconductor layer 24 is a porous layer which consists of a semiconductor particle s, the opening was formed between the semiconductor particles s and the charge transportation material t has permeated this opening. The charge transportation material t consists of the same component as the material used for the charge transporting bed 18. Under the

conductive layer 12, the substrate 28 is arranged on the substrate 26 and the counter electrode conductive layer 20. Substrates 26 and 28 may be for giving intensity, and may not be in an optoelectric transducer. Moreover, on the boundary of each layer, for example, the boundary of a conductive layer 12 and a photosensitive layer 16, the boundary of a photosensitive layer 16 and the charge transporting bed 18, and the boundary of the charge transporting bed 18 and the counter electrode conductive layer 20, the constituents of each class may be carrying out diffusive mixing mutually. In addition, a conductive layer 12, a substrate 26, and/or the counter electrode conductive layer 20 and substrate 28 of the side which may carry out incidence of the light to an optoelectric transducer 10 from either or both sides, and carries out incidence of the light to it can consist of material which has light-transmission nature, respectively.

[0067] Next, an operation of an optoelectric transducer 10 is explained. In addition, the case where the semiconductor particle *s* is *n* type is explained. If light carries out incidence to an optoelectric transducer 10, the light which carried out incidence will reach a photosensitive layer 16, will be absorbed with coloring matter *d* etc., and will generate the coloring matter *d* of an excitation state. The excited coloring matter *d* passes the electron of a high energy to the conduction band of the semiconductor particle *s*, and it becomes an oxidant itself. The electron from which it moved to the aforementioned conduction band reaches a conductive layer 12 by the network of the semiconductor particle *s*. Therefore, a conductive layer 12 has an electronegative potential to the counter electrode conductive layer 20. In the mode which used the optoelectric transducer 10 for the photoelectric cell, if this photoelectric cell is connected with an external circuit, the electron in a conductive layer 12 will reach the counter electrode conductive layer 20, working in an external circuit. The generated reductant (for example, I_3^-) returns the oxidant of coloring matter *d*, and returns an electron while it returns this electrolyte component (for example, I^-), when charge transportation material is an electrolyte. By continuing irradiating light, a series of reactions occur succeedingly and can take out the electrical and electric equipment.

[0068] Hereafter, an usable material and its formation method are explained to each class of the aforementioned optoelectric transducer. In addition, below, when calling it "a conductive base material", it is accepted conductive-layer 12, and although it consists of a conductive layer 12 and a substrate 26 which it is arbitrary and is prepared, when calling it a "counter electrode" including both sides, it is accepted counter electrode conductive-layer 20, and both sides are included although it consists of a counter electrode conductive layer 20 and a substrate 28 which it is arbitrary and is prepared.

[0069] (A) A conductive base material conductivity base material consists of the monolayer of (1) conductive layer or (2) conductive layers, and two-layer [of a substrate]. In the case of (1), material at which intensity and sealing performance are fully maintained as a conductive layer is used, for example, a metallic material (alloys containing these, such as platinum, gold, silver, copper, zinc, titanium, and aluminum) can be used. In the case of (2), the substrate which has the conductive layer which contains an electric conduction agent in a photosensitive-layer side can be used. As a desirable electric conduction agent, a metal (for example, alloys containing these, such as platinum, gold, silver, copper, zinc, titanium, aluminum, and an indium), carbon, or conductive metallic oxides (what doped a fluorine or antimony to an indium-tin multiple oxide and the tin oxide) are mentioned. The thickness of a conductive layer has desirable about 0.02-10 micrometers.

[0070] A conductive base material is so good that surface electrical resistance is low. The ranges of desirable surface electrical resistance are below 50ohms / **, and are below 20ohms / ** still more preferably.

[0071] When irradiating light from a conductive base material side, as for a conductive base material, it is desirable that it is substantially transparent. It means substantially that permeability is it 10% or more that it is transparent in some or the whole region of light of a visible - near infrared region (400-1200nm), it is desirable that it is 50% or more, and 80% or more is more desirable. It is desirable that the permeability of the wavelength region where a photosensitive layer has sensitivity especially is high.

[0072] What formed the transparent conductive layer which consists of a conductive metallic oxide in the front face of transparent substrates, such as glass or plastics, by an application or vacuum

evaporation as a transparent conductivity base material is desirable. A thing desirable as a transparent conductive layer is the 2 tin oxide or indium-stannic-acid ghost (ITO) which doped a fluorine or antimony. A transparent polymer film besides glass substrates, such as an advantageous soda glass and an alkali free glass without the influence of alkali elution, can be used for a transparent substrate in respect of a low cost and intensity. As a material of a transparent polymer film, there is a triacetyl-cellulose (TAC), polyethylene-terephthalate (PET), polyethylenenaphthalate (PEN), syndiotactic polystyrene (SPS), polyphenylene-sulfide (PPS), polycarbonate (PC), polyarylate (PAr), polysulfone (PSF), polyester sulfone (PES), polyimide (PI), polyether imide (PEI), annular polyolefine, and bromine-ized phenoxy etc. In order to secure sufficient transparency, as for the coverage of a conductive metallic oxide, it is desirable to consider as per [0.01-100g] two 1m of base materials of glass or plastics.

[0073] It is desirable to use a metal lead in order to lower resistance of a transparent conductivity base material. The quality of the material of a metal lead has desirable metals, such as platinum, gold, nickel, titanium, aluminum, copper, and silver. As for a metal lead, it is desirable to install in a transparent substrate by vacuum evaporation, sputtering, etc., and to prepare on it the transparent conductive layer which consists of the conductive tin oxide or a conductive ITO film. The fall of the amount of incident lights by metal lead installation may be 1 - 5% more preferably less than 10%.

[0074] (B) The photosensitive-layer aforementioned photosensitive layer absorbs light, performs charge separation, and has the function which produces an electron and an electron hole. The aforementioned photosensitive layer contains the semiconductor by which coloring matter sensitization was carried out. With the semiconductor by which coloring matter sensitization was carried out, generating of an optical absorption, the electron by this, and an electron hole takes place mainly in coloring matter, and a semiconductor bears the role which receives and transmits this electron (or electron hole). As for the semiconductor used by this invention, it is desirable that it is the n-type semiconductor which gives an anode current by a conductor electron serving as a carrier under optical pumping.

[0075] (1) The compounds (for example, a strontium titanate, titanate-acid calcium, titanate-acid sodium, a barium titanate, a niobic-acid potassium, etc.) which have silicon, an element semiconductor like germanium, a III-V system compound semiconductor, metal chalcogenide (for example, an oxide, a sulfide, selenides, or those composites etc.), or a perovskite structure as a semiconductor semiconductor can be used.

[0076] As chalcogenide of a desirable metal, the oxide of titanium, tin, zinc, iron, a tungsten, a zirconium, a hafnium, strontium, an indium, a cerium, an yttrium, a lanthanum, vanadium, niobium, or a tantalum, cadmium, zinc, lead, silver, antimony or the sulfide of a bismuth, cadmium or a leaden selenide, the telluride of cadmium, etc. are mentioned. As other compound semiconductors, the selenide of phosphides, such as zinc, a gallium, an indium, and cadmium, a gallium arsenide, or a copper-indium, the sulfide of a copper-indium, etc. are mentioned. Furthermore, the composite expressed with $MxOySz$ or $M1xM2yOz$ (the number [metallic element] of combination with which an oxygen atom, x, and y and z become as for M, M1, and M2, and, as for O, a valence becomes neutral, respectively) can also be used preferably.

[0077] The desirable example of the semiconductor used for this invention Si, TiO_2 , SnO_2 , Fe_2O_3 , WO_3 , ZnO , Nb_2O_5 , CdS , ZnS and PbS , Bi_2S_3 , $CdSe$, $CdTe$, They are $SrTiO_3$, GaP , InP , $GaAs$, $CuInS_2$, and $CuInSe_2$ grade. More preferably TiO_2 , ZnO , SnO_2 , Fe_2O_3 , WO_3 , Nb_2O_5 , CdS , It is PbS , $CdSe$, $SrTiO_3$ and InP , $GaAs$, and $CuInS_2$ and $CuInSe_2$, is TiO_2 and Nb_2O_5 especially preferably, and is TiO_2 most preferably. TiO_2 which includes an anatase type crystal 70% or more is desirable especially desirable, and TiO_2 is TiO_2 of 100% anatase type crystal. Moreover, it is the purpose which raises the electronic conductivity in these semiconductors, and it is also effective to dope a metal. As a metal to dope, divalent and a trivalent metal are desirable. It is the purpose which prevents that a reverse current flows from a semiconductor to a charge transporting bed, and it is also effective to dope a univalent metal to a semiconductor.

[0078] Although a single crystal or a polycrystal is sufficient as the semiconductor used for this invention, from viewpoints, such as a manufacturing cost, raw-material reservation, and an energy pay back time, a polycrystal is desirable and especially the porous membrane that consists of a

semiconductor particle is desirable. Moreover, the amorphous portion may be included in part.

[0079] Although the particle size of a semiconductor particle is generally the order of nm- μ m, as for the mean particle diameter of the primary particle which asked for projected area from the diameter when converting into a circle, it is desirable that it is 5-200nm, and its 8-100nm is more desirable. Moreover, the mean particle diameter of the semiconductor particle in dispersion liquid (aggregated particle) has desirable 0.01-30 micrometers. It is 10nm or less preferably [may mix two or more kinds of particles from which a particle size distribution differs, and / that the average size of a small particle is 25nm or less in this case], and more preferably. Particle size is big, for example, it is also desirable to mix a semiconductor particle (100nm or more and about 300nm) in order to scatter an incident light and to raise the rate of optical capture.

[0080] You may be two or more sorts of mixtures from which the kind of semiconductor particle also differs. When mixing and using two or more sorts of semiconductor particles, as for one sort, it is desirable that they are TiO₂, ZnO, Nb₂O₅, or SrTiO₃. Moreover, it is desirable that they are SnO₂, Fe₂O₃, or WO₃ as one more sort. As a still more desirable combination, combination, such as ZnO, SnO₂, ZnO and WO₃, or ZnO, SnO₂, WO₃, can be mentioned. When mixing and using two or more sorts of semiconductor particles, each particle size may differ. The particle size of the semiconductor particle mentioned especially at the one above-mentioned item is large, and combination with the small semiconductor particle mentioned henceforth [2 items] is desirable. The particle of a desirable large particle size is 100nm or more, and the particle of a small particle size is 15nm or less in combination.

[0081] a sol-gel method given [as a method of producing a semiconductor particle] in "the thin-layer-coating technology by the sol-gel method" (1995) etc. of the company (1998) of the "science of sol-gel method" AGUNE ** style of *****, and a technical-information association, and "composition of the monodisperse particle by the new synthesis method gel-sol method and size gestalt control" of Tadao Sugimoto -- wait -- ****, the 35th volume, No. 9, and the gel-sol method of a 1012-1018 pages (1996) publication Moreover, the method of producing an oxide for the chloride which Degussa developed by elevated-temperature hydrolysis in an acid hydrogen salt is also desirable.

[0082] Although each of above-mentioned sol-gel methods, gel-sol methods, and elevated-temperature adding-water part solution methods in the inside of the acid hydrogen salt of a chloride is desirable when a semiconductor particle is titanium oxide, the sulfuric-acid method and chlorine method of a publication can also be further used for "titanium oxide physical-properties and applied-technology" Gihodo Shuppan Co., Ltd. (1997) of the Seino study. The method of Barbe's and others journal OBU American ceramic society, the 80th volume, No. 12, and a 3157-3171 pages (1997) publication and the method of Burnside's and others chemistry OBU MATERIARUZU, the 10th volume, No. 9, and a 2419-2425-page publication are also still more desirable as a sol-gel method.

[0083] (2) The semiconductor particle layer aforementioned semiconductor is used with the gestalt of the semiconductor particle layer formed for example, on the aforementioned conductive base material. In order to apply a semiconductor particle on a conductive base material, the above-mentioned sol-gel method etc. can also be used besides the method of applying the dispersion liquid or the colloidal solution of a semiconductor particle on a conductive base material. When mass-production-izing of an optoelectric transducer, the physical properties of semiconductor particle liquid, the versatility of a conductive base material, etc. are taken into consideration, the wet film production method is comparatively advantageous. As the wet film production method, the applying method, print processes, an electrolytic-deposition method, and an electrodeposition process are typical. Moreover, the SPD method which sprays the metallic-oxide precursor pyrolyzed on the method of carrying out vacuum evaporatio by the method (the LPD method) of depositing by the liquid phase by the ligand exchange etc., the spatter, etc., CVD, or the warmed substrate from the method of oxidizing a metal and a metal solution, and forms a metallic oxide can also be used.

[0084] In case the method of distributing while grinding using the method and mill which are mashed with the mortar other than the above-mentioned sol-gel method as a method of producing the dispersion liquid of a semiconductor particle, or a semiconductor is compounded, the method of depositing as a particle and using it as it is in a solvent, etc. is mentioned.

[0085] As a dispersion medium, water or various kinds of organic solvents (for example, a methanol, ethanol, isopropyl alcohol, a citronellol, terpineol, a dichloromethane, an acetone, an acetonitrile, ethyl acetate, etc.) are mentioned. You may use polymer like a polyethylene glycol, a hydroxyethyl cellulose, and a carboxymethyl cellulose, a surfactant, an acid, or a chelating agent as a distributed assistant if needed in the case of distribution. Since the semiconductor layer which regulation of the viscosity of dispersion liquid is attained and cannot separate further easily due to changing the molecular weight of a polyethylene glycol can be formed or the voidage of a semiconductor layer can be controlled, it is desirable to add a polyethylene glycol.

[0086] As the method of application, the slide hopper method given in application and the wire bar methods currently indicated by JP,58-4589,B as that by which metering is made into the same portion, such as the air knife method and the blade method, U.S. JP,2681294,B, said 2761419 numbers, said 2761791 numbers, etc., the extrusion method, the curtain method, etc. are desirable as metering systems, such as a roller and the dipping method, as an application system. Moreover, the spin method and a spray method are also desirable as a general aviation. As the wet printing method, letterpress, offset, and the three major print processes of gravure are begun, and intaglio printing, the rubber version, screen-stencil, etc. are desirable. According to liquid viscosity or wet thickness, the desirable film production method is chosen from these.

[0087] The layer of a semiconductor particle can carry out the multilayer application of the dispersion liquid of the semiconductor particle from which not only a monolayer but particle size is different, or can also carry out the multilayer application of the application layer containing the semiconductor particle (or a different binder, a different additive) from which a kind differs. When thickness is insufficient, the multilayer application is effective at a one-time application.

[0088] Since the amount of support coloring matter per unit projected area increases so that semiconductor particle layer thickness (it is the same as the thickness of a photosensitive layer) generally becomes thick, although the rate of capture of light becomes high, since the generated diffusion length of electron increases, the loss by charge reunion also becomes large. Therefore, the thickness with a desirable semiconductor particle layer is 0.1-100 micrometers. When using for a photoelectric cell, semiconductor particle layer thickness has desirable 1-30 micrometers, and its 2-25 micrometers are more desirable. The coverage which receives per two 1m of base materials of a semiconductor particle has 0.5-desirable 100g, and 3-its 50g are more desirable.

[0089] Heat-treating is desirable, in order to raise improvement in paint film intensity, and adhesion with a base material, while contacting semiconductor particles electronically, after applying a semiconductor particle on a conductive base material. The range of desirable heating temperature is 40 degrees C or more 700 degrees C or less, and is 100 degrees C or more 600 degrees C or less more preferably. Moreover, heating time is 10 minutes - about 10 hours. When using the low base material of the melting point or softening temperature like a polymer film, high temperature processing is not desirable in order to cause degradation of a base material. Moreover, it is desirable that it is low temperature (for example, 50-350 degrees C) as much as possible also from the viewpoint of cost. Low temperature-ization can also be performed by becoming possible by the small semiconductor particle 5nm or less, heat-treatment under existence of a mineral acid and a metallic-oxide precursor, etc., and impressing irradiation of ultraviolet rays, infrared radiation, microwave, etc., electric field, and an ultrasonic wave. It is desirable to use together for the purpose which removes the unnecessary organic substance etc. simultaneously, combining suitably heating besides the above-mentioned irradiation or impression, reduced pressure, oxygen plasma treatment, pure water washing, solvent cleaning, gas scrubbing, etc.

[0090] It is the purpose which the surface area of a semiconductor particle is increased, or raises the purity near the semiconductor particle after heat-treatment, and raises the electron-injection efficiency from coloring matter to a semiconductor particle, for example, chemical-plating processing using titanium-tetrachloride solution and electrochemical plating processing using titanium-trichloride solution may be performed. Moreover, it is the purpose which prevents that a reverse current flows from a semiconductor particle to a charge transporting bed, and it is effective to also make the low organic substance of electronic conductivity other than coloring matter stick to a particle front face. The object which has a hydrophobic radical as the organic substance made to adsorb is desirable.

[0091] As for a semiconductor particle layer, it is desirable to have a large surface area so that much coloring matter can be adsorbed. As for the surface area in the state where the layer of a semiconductor particle was applied on the base material, it is desirable that they are 10 or more times to projected area, and it is desirable that they are further 100 or more times. Although especially a limit does not have this upper limit, they are usually about 1000 times.

[0092] (3) If it is the compound which can carry out sensitization of the semiconductor, the sensitizing dye used for a coloring matter photosensitive layer has absorption in a visible region or a near-infrared region, and can use it for arbitration, and organometallic complex coloring matter, methine coloring matter, porphyrin system coloring matter, and its phthalocyanine system coloring matter are desirable. Moreover, since the wavelength region of photo electric translation is made large as much as possible and a conversion efficiency is gathered, two or more kinds of coloring matter can be used together or mixed. In this case, the coloring matter used together or mixed and its rate can be chosen so that it may double with the target wavelength region and intensity distribution of the light source.

[0093] As for such coloring matter, it is desirable to have the suitable joint machine (interlocking group) which has the adsorption capacity force to the front face of a semiconductor particle. The chelation machine which has pi conductivity like a COOH basis, OH basis, SO₃H set, -P(O) (OH)₂ set and an acidic group like -OP(O) (OH)₂ set or an oxime, dioxime, a hydroxyquinoline, salicylate, or alpha-KETOENO rate as a desirable joint machine is mentioned. A COOH basis, -P(O) (OH)₂ set, and especially -OP(O) (OH)₂ set are desirable especially. These bases may form alkali metal etc. and the salt, and may form the inner salt. Moreover, when it contains an acidic group like [in case a methine chain forms a squarylium ring and a crocodile NIUMU ring] in the case of poly methine coloring matter, you may have this portion as a joint machine.

[0094] Hereafter, the desirable sensitizing dye used for a photosensitive layer is explained concretely.

(a) When organometallic complex coloring matter coloring matter is metal complex coloring matter, metal phthalocyanine dye, metalloporphyrin coloring matter, and ruthenium complex coloring matter are desirable, and especially ruthenium complex coloring matter is desirable. as ruthenium complex coloring matter -- for example, U.S. JP,4927721,B -- said -- No. 4684537 -- said -- No. 5084365 -- said -- No. 5350644 -- said -- No. 5463057 -- said -- the complex coloring matter of a publication is mentioned to each official report, such as each specification, such as No. 5525440, and JP,7-249790,A, ***** No. 504512 [ten to], the world patent 98/No. 50393, and JP,2000-26487,A

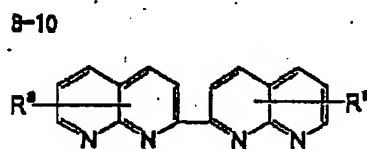
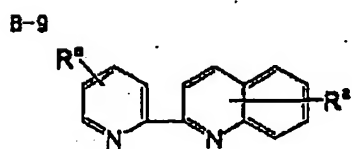
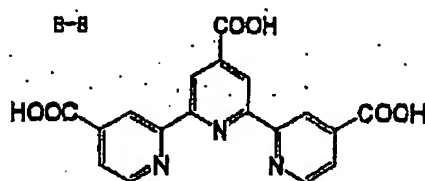
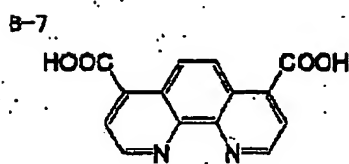
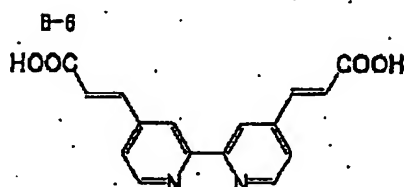
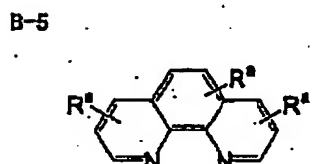
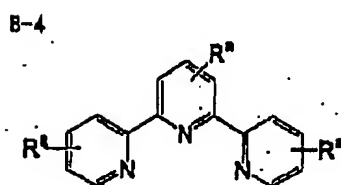
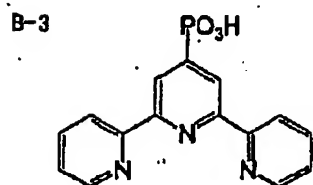
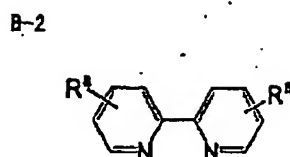
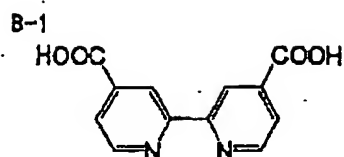
[0095] When the aforementioned coloring matter is furthermore ruthenium complex coloring matter, the ruthenium complex coloring matter expressed with the following general formula (IV) is desirable.

General formula (IV)

(A1) A1 expresses the ligand of 1 or 2 seats among the tRu(B-a) u(B-b) v(B-c) w aforementioned general formula (IV). As for A1, it is desirable that it is the ligand chosen from the group which consists of a derivative of Cl, SCN, H₂O, Br, I, CN and NCO, SeCN, alpha-diketones, oxalic acid, and a dithiocarbamic acid. When t is two or more, even if two or more A1 is the same, it may differ. B-a, B-b, and B-c express the ligand independently expressed with the following formula (B-1) - (B-10) either, respectively among the aforementioned general formula (IV). t expresses the integer of either 0-3, and u, v, and w are together put suitably according to the kind of ligand so that the ruthenium complex which expresses 0 or 1 respectively and is expressed with the aforementioned general formula (IV) may turn into six coordinated complexes.

[0096]

[Formula 12]

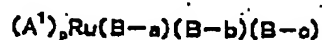


[0097] Among aforementioned formula (B-1) - (B-10), R^a expresses a hydrogen atom or a substituent and the aryl group which is not replaced [the substitution of the aralkyl machine which is not replaced / the substitution of the alkyl group which is not replaced / the substitution of a halogen atom and the carbon atomic numbers 1-12 or / and the carbon atomic numbers 7-12 or / and the carbon atomic numbers 6-12 or], an acidic group (these acidic groups may form the salt), or a chelation machine is mentioned as The shape of a straight chain and the letter of branching are sufficient as the alkyl portions of an alkyl group and an aralkyl machine. Moreover, a monocycle or a polycyclic (the condensed ring, ring set) is sufficient as the aryl portions of the aforementioned aryl group and an aralkyl machine. Among the aforementioned general formula (IV), even if B-a, B-b, and B-c are the same, they may differ.

[0098] Although the desirable example (instantiation compound R-1-17) of organometallic complex coloring matter is shown below, the coloring matter used for this invention is not limited to the following examples.

[0099]

[Formula 13]



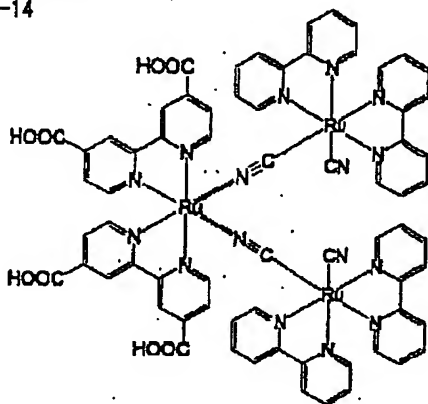
	A^1	p	B-a	B-b	B-c	R^a
R-1	SCN	2	B-1	B-1	—	—
R-2	CN	2	B-1	B-1	—	—
R-3	Cl	2	B-1	B-1	—	—

R-4	CN	2	B-7	B-7	-	-
R-5	SCN	2	B-7	B-7	-	-
R-6	SCN	2	B-1	B-2	-	H
R-7	SCN	1	B-1	B-3	-	-
R-8	Cl	1	B-1	B-4	-	H
R-9	I	2	B-1	B-5	-	H
R-10	SCN	3	B-8	-	-	-
R-11	CN	3	B-8	-	-	-
R-12	SCN	1	B-2	B-8	-	H
R-13	-	0	B-1	B-1	B-1	-

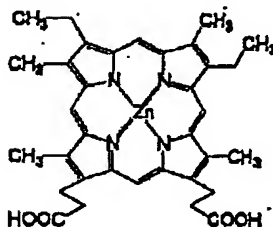
[0100]

[Formula 14]

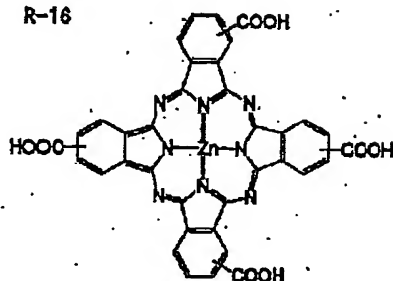
R-14



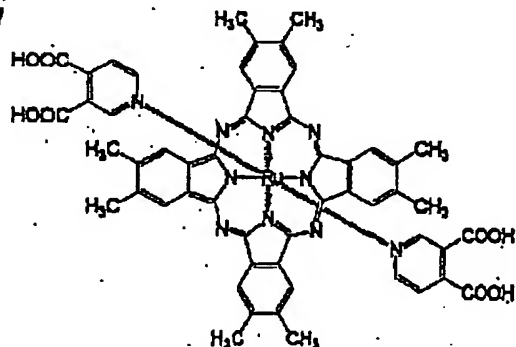
R-15



R-16



R-17



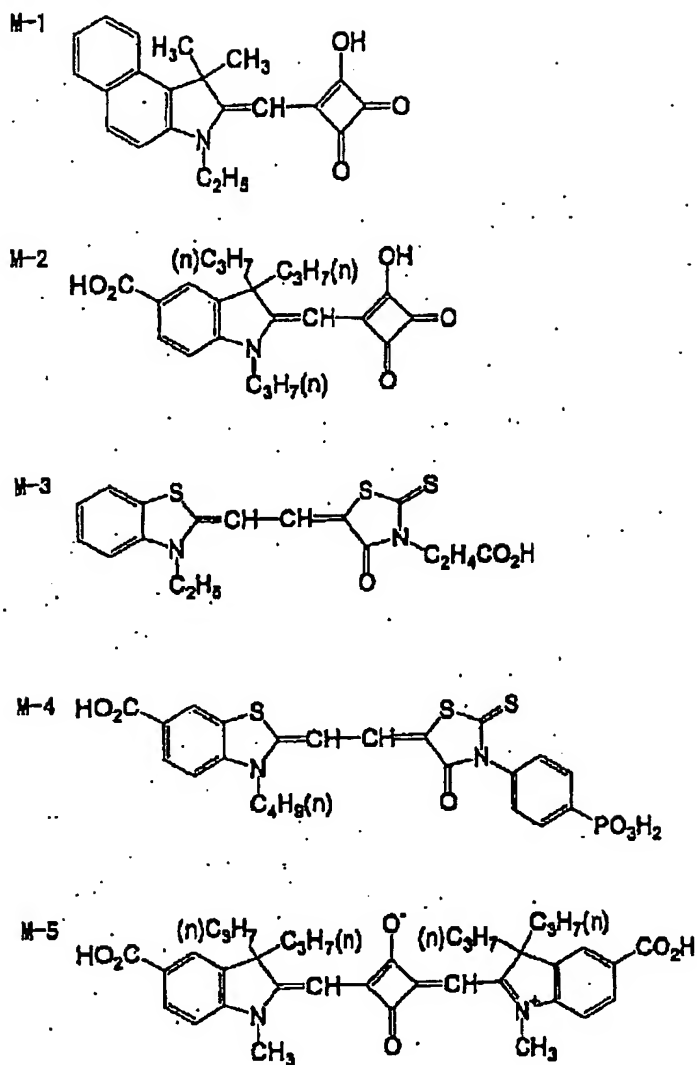
[0101] (b) The desirable methine coloring matter used for a methine coloring matter this invention is poly methine coloring matter, such as a cyanine dye, merocyanine coloring matter, and SUKUWARIRIUMU coloring matter. As poly methine coloring matter preferably used by this invention, the coloring matter of a publication is mentioned in each specification of JP,11-35836,A, JP,11-67285,A, JP,11-86916,A, JP,11-97725,A, JP,11-158395,A, JP,11-163378,A, JP,11-214730,A, JP,11-214731,A, JP,11-238905,A, JP,2000-26487,A, the Europe patent No. 892411, said 911841 numbers, and said 991092 numbers, for example. The example of desirable methine coloring matter

http://www4.ipdl.jpo.go.jp/cgi-bin/tran_web.cgi_ejje

is shown below.

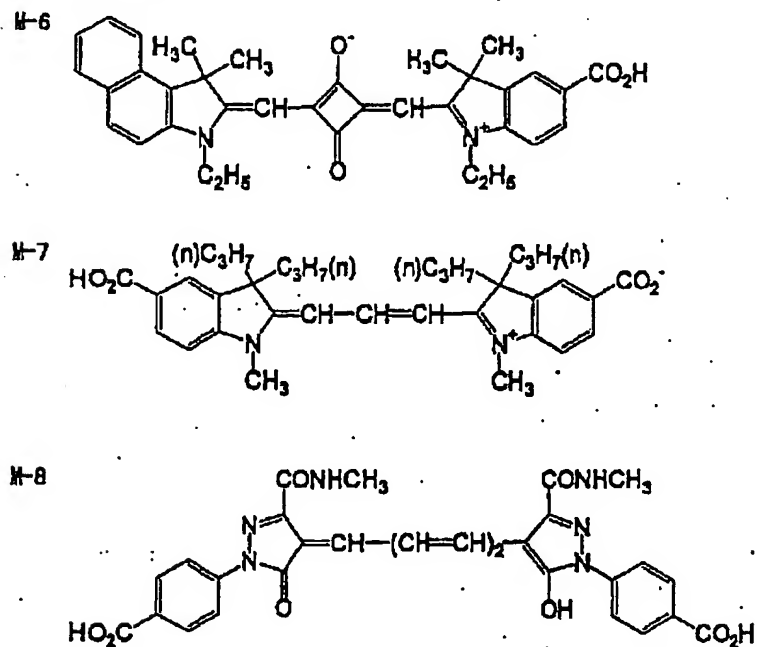
[0102]

[Formula 15]



[0103]

[Formula 16]

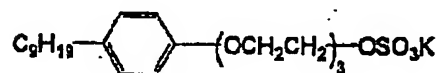
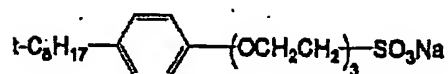


[0104] (4) In order to make coloring matter stick to the adsorption semiconductor particle of the coloring matter to a semiconductor particle, the method which is immersed in the conductive base material which has the semiconductor particle layer dried well in the solution of coloring matter, or applies the solution of coloring matter to a semiconductor particle layer can be used. In the case of the former, dip coating, the dipping method, a roller, the air knife method, etc. are usable. In the case of dip coating, adsorption of coloring matter may be performed at a room temperature, and you may perform it by carrying out heating reflux as indicated by JP,7-249790,A. Moreover, as the latter method of application, there are the wire bar method, the slide hopper method, the extrusion method, the curtain method, the spin method, a spray method, etc. one desirable as a solvent which dissolves coloring matter -- for example, alcohols (a methanol --) nitril (an acetonitrile --), such as ethanol, t-butanol, and benzyl alcohol Nitromethanes, such as a propionitrile and 3-methoxy propionitrile, a halogenated hydrocarbon (a dichloromethane, a dichloroethane, and chloroform --) Ether, such as a chlorobenzene (diethylether, tetrahydrofuran, etc.), dimethyl sulfoxide and amides (N.N-dimethylformamide --) N-methyl pyrrolidones, such as N and N-dimethyl acetamido, 1, 3-dimethyl imidazolidinone, 3-methyl oxazolidinone and ester (ethyl acetate, butyl acetate, etc.) Carbonates (diethyl carbonate, an ethylene carbonate, propylene carbonate, etc.), ketones, hydrocarbons (an acetone, 2-butanone, cyclohexanone, etc.) (Korean geisha, the petroleum ether, benzene, toluene, etc.), and these mixed solvents are mentioned.

[0105] All the amounts of adsorption of coloring matter have desirable per [a unit surface area (1m²) / 0.01] - 100mmol of a porosity semiconductor-electrode substrate. Moreover, as for the amount of adsorption to the semiconductor particle of coloring matter, it is desirable that it is the range per [0.01] 1g of semiconductor particles - of 1mmol. The sensitization effect in a semiconductor is fully acquired by considering as the coloring matter amount of adsorption of the aforementioned range. On the other hand, if there is too little coloring matter, the sensitization effect will become inadequate, and if there is too much coloring matter, the coloring matter which has not adhered to a semiconductor will float, and it becomes the cause of reducing the sensitization effect. In order to increase the amount of adsorption of coloring matter, heat-treating before adsorption is desirable. After heat-treatment, in order to avoid that water sticks to a semiconductor particle front face, it is desirable to perform adsorption operation of coloring matter quickly [while the temperature of a semiconductor-electrode substrate is 60-150 degrees C], without returning to ordinary temperature. Moreover, for the purpose which reduces interactions, such as condensation between coloring matter, a colorless compound may be added to coloring matter and a coadsorption may be carried out to a semiconductor particle. The sulfonates like a steroid compound (for example, chenodeoxycholic acid) or the following example which the effective compound for this purpose is a compound with a surface activity property and structure, for example, have a carboxyl group are mentioned.

[0106]

[Formula 17]



[0107] As for non-adsorbed coloring matter, it is desirable that washing removes promptly after adsorption. It is desirable to use a wet washing tub and to wash by organic solvent like polar solvents, such as an acetonitrile, and an alcohols solvent. After adsorbing coloring matter, amines and the 4th class salt may be used and the front face of a semiconductor particle may be processed. As desirable amines, a pyridine, a 4-t-butyl pyridine, a polyvinyl pyridine, etc. are mentioned, and tetrabutylammonium iodide, tetrapod hexyl ammonium iodide, etc. are mentioned as the desirable 4th class salt. When these are liquids, it may use as it is, and you may dissolve and use for an organic solvent.

solvent.

[0108] (C) A charge transporting-bed charge transporting bed is a layer containing the charge transportation material which has the function to supplement the oxidant of coloring matter with an electron. the solution (electrolytic solution) which the ion of a redox couple dissolved as a (i) ion-transport material as an example of a typical charge transportation material which can be used for this charge transporting bed, the so-called gel electrolyte which sank the solution of a redox couple into the gel of a polymer matrix, and the quality of molten salt electrolysis containing a oxidation reduction counter ion -- a solid electrolyte is mentioned further Moreover, carrier movement in the (ii) solid-state can also use electronic transportation material and electron hole (hole) transportation material as a charge transportation material [other than the charge transportation material with which ion is concerned]. In this invention, although the electrolyte constituent of this invention is used for this charge transporting bed, the above-mentioned charge transportation material other than this can also be used together.

[0109] (1) Two kinds of methods can be considered about the formation method of the formation charge transporting bed of a charge transporting bed. One is the method of sticking a counter electrode previously on a photosensitive layer, and putting a liquefied charge transporting bed between the gap. Another is the method of giving a charge transporting bed directly on a photosensitive layer, and a counter electrode will be given after that.

[0110] In the case of the former, the ordinary-pressure process which uses the capillarity by being immersed etc. as how to put a charge transporting bed, or the vacuum process which makes it a low pressure and replaces the gaseous phase of a gap by the liquid phase from an ordinary pressure can be used.

[0111] In the case of the latter, in a wet charge transporting bed, a counter electrode will be given with not drying, and the liquid disclosure prevention measure of the edge section will be taken. Moreover, in the case of a gel electrolyte, there is a method of applying with wet and solidifying by methods, such as a polymerization, and a counter electrode can also be given after drying and fixing in that case. As a method of giving wet organic electron hole transportation material besides the electrolytic solution, and a gel electrolyte, the same method as grant of the above-mentioned semiconductor particle layer or coloring matter can be used.

[0112] (D) Like the aforementioned conductive base material, the monolayer structure of a counter electrode conductive layer which consists of a conductive material is sufficient as a counter electrode counter electrode, and it may consist of a counter electrode conductive layer and a support substrate. As electric conduction material used for a counter electrode conductive layer, a metal, carbon (for example, platinum, gold, silver, copper, aluminum, magnesium, an indium, etc.), or conductive metallic oxides (an indium-tin multiple oxide, fluorine dope tin oxide, etc.) are mentioned. Also in this, platinum, gold, silver, copper, aluminum, and magnesium can be preferably used as a counter electrode conductive layer. The example of the desirable support substrate of a counter electrode is glass or plastics, and the vacuum evaporatio of it is applied or carried out, and it uses the above-mentioned electric conduction agent for this. Although especially the thickness of a counter electrode conductive layer is not restricted, 3nm - 10 micrometers are desirable. The surface electrical resistance of a counter electrode conductive layer is as good as a low. As a range of desirable surface electrical resistance, it is below 50ohms / **, and they are below 20ohms / ** still more preferably.

[0113] Since light may be irradiated from both a conductive base material, and both [either or], in order for light to reach a photosensitive layer, it is good if at least one side of a conductive base material and a counter electrode is substantially transparent. It is desirable to make a conductive base material transparent from a viewpoint of improvement in a generating efficiency, and to carry out incidence of the light from a conductive base material side. In this case, as for a counter electrode, it is desirable to have the property to reflect light. As such a counter electrode, the glass which deposited the metal or the conductive oxide, plastics, or a metal thin film can be used.

[0114] A counter electrode should just stick the application, plating, or counter electrode conductive-layer side of the substrate which carries out vacuum evaporatio (PVD, CVD), or has a counter electrode conductive layer for direct electric conduction material on a charge transporting bed. Moreover, as well as the case of a conductive base material when especially a counter electrode is

transparent, it is desirable to use a metal lead in order to lower resistance of a counter electrode. In addition, the fall of the desirable quality of the material of a metal lead and the desirable installation method, and the amount of incident lights by metal lead installation etc. is the same as the case of a conductive base material.

[0115] (E) In order to prevent other layer counter electrodes and the short circuit of a conductive base material, it is desirable to paint the thin film layer of a precise semiconductor as an under coat between a conductive base material and a photosensitive layer beforehand, and it is effective especially when using electronic transportation material and electron hole transportation material for a charge transporting bed. TiO_2 , SnO_2 , Fe_2O_3 , and WO_3 , ZnO and Nb_2O_5 are desirable as an under coat, and it is TiO_2 still more preferably. An under coat can be painted by the spatter besides the spray pyrolysis method indicated by *Electrochim. Acta* 40,643-652 (1995) etc. The desirable thickness of an under coat is 5-1000nm, and its 10-500nm is still more desirable.

[0116] Moreover, you may prepare functional layers, such as a protective layer and an acid-resisting layer, between one side of the conductive base material which acts as an electrode, and a counter electrode or both outside front faces, a conductive layer, and substrates, or in the middle of a substrate. According to the quality of the material, the applying method, a vacuum deposition, the sticking method, etc. can be used for formation of these functional layers.

[0117] In order to prevent said degradation of each structure and vaporization of contents, as for the photoelectrochemical cell of this invention, it is desirable to seal the side with polymer, adhesives, etc.

[0118] The photoelectrochemical cell of this invention is the same composition as the aforementioned optoelectric transducer fundamentally, it connects the aforementioned optoelectric transducer to an external circuit through lead wire etc., and it constitutes it so that it may be made to work in an external circuit. The external circuit itself connected to the aforementioned conductive base material and the aforementioned counter electrode through lead wire etc. can use a well-known thing. Moreover, the photoelectrochemical cell of this invention can take the same module structure as fundamentally as the conventional solar cell module. Although the structure of a cell being constituted on support substrates, such as a metal and a ceramic, and the aforementioned solar cell module covering a it top with a restoration resin, cover glass, etc. generally, and incorporating light from the opposite side of a support substrate is taken, it is also possible to consider as the structure of using transparent materials, such as tempered glass, for a support substrate, constituting a cell on it, and incorporating light from the transparent support substrate side. The substrate one apparatus module structure specifically used with the module structure called a super straight type, a substrate type, and potting type, an amorphous-silicon solar cell, etc. is known, and the photoelectrochemical cell of this invention can also choose such module structures suitably according to the purpose of use, a service space, and environment. Specifically, it is desirable to apply the structure and the mode of a publication to JP,2000-268892,A.

[0119] The non-water rechargeable battery of this invention which used the electrolyte constituent of this invention below for the [non-water rechargeable battery] is explained. The non-water rechargeable battery of this invention is characterized by including the electrolyte constituent of this invention. The non-water rechargeable battery of this invention shows the outstanding cycle nature, without reducing capacity greatly, since the electrolyte constituent of this invention is contained.

[0120] Although the transition-metals oxide which can insert and emit a lithium ion in reversible is sufficient as a positive active material when using the electrolyte constituent of this invention for a non-water rechargeable battery, a lithium content transition-metals oxide is especially desirable. As a desirable lithium content transition-metals oxide positive active material used by this invention, an oxide including the lithium content Ti, V, Cr, Mn, Fe, Co, nickel, Cu, Mo, and W is mentioned. Moreover, you may mix alkali metal other than a lithium (element of the 1st (IA) group of a periodic table, and the 2nd (IIA) group), aluminum, Ga, In, germanium, Sn, Pb, Sb, Bi, Si, P, B, etc. 0-30-mol% of the amount of mixtures is desirable to transition metals.

[0121] It is more desirable to mix and compound so that the mole ratio of the sum total of a lithium compound / transition-metals compound (at least one sort chosen from Ti, V, Cr, Mn, Fe, Co, nickel, Mo, and W with transition metals here) may be set to 0.3-2.2 as a desirable lithium content transition-

metals oxide positive active material rather than being used by this invention.

[0122] As an especially desirable lithium content transition-metals oxide positive active material with which it is used by this invention, it is desirable to mix and compound so that the mole ratio of the sum total of a lithium compound / transition-metals compound (at least one sort chosen from V, Cr, Mn, Fe, Co, and nickel with transition metals here) may be set to 0.3-2.2.

[0123] Especially the desirable lithium content transition-metals oxide positive active material used by this invention LigM 3O₂ (M3 is chosen from Co, nickel, Fe, and Mn -- one or more sorts) It is the material containing g=0-1.2, or the material which has the Spinel structure expressed with Li_hM 42O₄ (M4 is Mn and h=0-2), and aluminum, Ga, In, germanium, Sn, Pb, Sb, Bi, Si, P, or B may be mixed as M3 and M4 in addition to transition metals. 0-30-mol% of the amount of mixtures is desirable to transition metals.

[0124] As most desirable lithium content transition-metals oxide positive active material used by this invention, LigCoO₂, LigNiO₂, LigMnO₂, LigCo_jNi_(1-j) O₂, and Li_hMn 2O₄ (it is g=0.02-1.2, j= 0.1 to 0.9, and h=0-2 here) are mentioned. Here, the above-mentioned g value is a value before a charge-and-discharge start, and is fluctuated by charge and discharge.

[0125] Although a positive active material is compoundable by well-known methods, such as the method of mixing a lithium compound and a transition-metals compound and calcinating, and a solution reaction, especially its calcinating method is desirable.

[0126] Although especially the average grain size of the positive active material used by this invention is not limited, 0.1-50 micrometers is desirable. Although not limited especially as a specific surface area, 0.01-50m²/g is desirable at a BET adsorption method. Moreover, as pH of the supernatant when melting 5g of positive active materials to 100ml of distilled water, 12 or less [7 or more] are desirable.

[0127] In order to make it a predetermined grain size, the grinder and classifier which were known well can be used. For example, a mortar, a ball mill, a vibration ball mill, a vibration mill, a satellite ball mill, a planet ball mill, a revolution air current type jet mill, a screen, etc. are used. After washing by water, acid solution, alkaline solution, and the organic solvent, you may use the positive active material obtained by baking.

[0128] One of the negative-electrode active materials used by this invention is a carbonaceous material in which occlusion discharge of a lithium is possible. Carbonaceous material is a material which consists of carbon substantially. For example, the carbonaceous material which calcinated various kinds of synthetic resin, such as artificial graphites, such as a petroleum pitch, a natural graphite, and a vapor-growth graphite, and a resin of a PAN system, and a furfuryl alcohol resin, can be mentioned. Furthermore, various carbon fibers, such as a PAN system carbon fiber, a cellulose system carbon fiber, a pitch based carbon fiber, a vapor-growth carbon fiber, a dehydration PVA system carbon fiber, a lignin carbon fiber, a vitrified carbon fiber, and an activated carbon fiber, a mesophase microsphere, a graphite whisker, a plate-like graphite, etc. can also be mentioned. Such carbonaceous material can also be divided into difficulty graphitized-carbon material and a graphite system carbon material according to the grade of graphitization. Moreover, as for carbonaceous material, it is desirable to have the spacing indicated by JP,62-22066,A, JP,2-6856,A, and the 3-45473 official report, density, and the size of a microcrystal. Carbonaceous material does not need to be a single material and the graphite which has the mixture of a natural graphite and an artificial graphite given in JP,5-90844,A and an enveloping layer given in JP,6-4516,A can also be used for it.

[0129] As other examples of an usable negative-electrode active material, an oxide and/or chalcogenide are mentioned to this invention. Especially an amorphous oxide and/or chalcogenide are desirable. It is the object which has the broadcloth dispersion band which has the peak to a 20 to 40 degrees field with 2theta value with the X-ray diffraction method ["be / amorphous / it"] here using CuK alpha rays, and you may have a crystalline diffraction line. Among the crystalline diffraction lines preferably looked at by 40 degrees or more 70 degrees or less with 2theta value, the strongest intensity is 100 or less times of the diffraction line intensity of the peak of the broadcloth dispersion band looked at by 20 degrees or more 40 degrees or less with 2theta value, is 5 or less times still more preferably, and is not having a crystalline diffraction line preferably especially.

[0130] In this invention, especially, the amorphous oxide of a semimetal element and/or chalcogenide

are desirable, and the element of the 13th (IIIB) group or a periodic table - 13 (VB) groups, independent of the oxide which consists of two or more sorts of those combination of aluminum, Ga, Si, Sn, germanium, Pb, Sb, and Bi, and chalcogenide are chosen.

[0131] For example, Ga₂O₃, SiO₂, GeO₂, SnO₂, SnO, PbO, PbO₂ and Pb₂O₃, Pb₂O₄, Pb₃O₄, Sb₂O₃, Sb₂O₄, Sb₂O₅, Bi₂O₃, Bi₂O₄, SnSiO₃, GeS, SnS, SnS₂, PbS and PbS₂, Sb₂S₃, Sb₂S₅, SnSiS₃, etc. are desirable. Moreover, these may be the multiple oxides 2 with a lithium oxide, for example, Li₂SnO.

[0132] In the negative-electrode material in this invention, the amorphous oxide consisting mainly of Sn, Si, and germanium is still more desirable, and it is desirable that it is the amorphous oxide expressed with the following general formula (V) especially.

General formula (V)

M1 among a SnM1dM2eOf general formula (V) The element more than a kind is expressed with being chosen out of aluminum, B, P, and germanium that it is few. The element more than a kind is expressed at least. M2 -- the [periodic-table] -- it is chosen out of 1(IA) group element, the 2nd (IIA) group element, the 3rd (IIIA) group element, and a halogen -- 0.2 or more numbers [two or less] and e express 0.2<d+e<2 with or more 0.01 one or less number, and, as for d, f expresses or more 1 six or less number.

[0133] As an amorphous oxide which makes Sn a subject, although the following compound is mentioned, for example, this invention is not necessarily limited to these.

C-1 SnSiO₃C-2 Sn_{0.8}Al_{0.2}B_{0.3}P_{0.2}Si_{0.5}O_{3.6}C-3 SnAl_{0.4}B_{0.5}Cs_{0.1}P_{0.5}O_{3.65}C-4

SnAl_{0.4}B_{0.5}Mg_{0.1}P_{0.5}O_{3.7}C-5 SnAl_{0.4}B_{0.4}Ba_{0.08}P_{0.4}O_{3.28}C-6

SnAl_{0.4}B_{0.5}Ba_{0.08}Mg_{0.08}P_{0.3}O_{3.26}C-7 SnAl_{0.1}B_{0.2}Ca_{0.1}P_{0.1}Si_{0.5}O_{3.1}C-8

SnAl_{0.2}B_{0.4}Si_{0.4}O_{2.7}C-9 SnAl_{0.2}B_{0.1}Mg_{0.1}P_{0.1}Si_{0.5}O_{2.6}C-10 SnAl_{0.3}B_{0.4}P_{0.2}Si_{0.5}O_{3.55}C-11

SnAl_{0.3}B_{0.4}P_{0.5}Si_{0.5}O_{4.3}C-12 SnAl_{0.1}B_{0.1}P_{0.3}Si_{0.6}O_{3.25}C-13

SnAl_{0.1}B_{0.1}Ba_{0.2}P_{0.1}Si_{0.6}O_{2.95}C-14 SnAl_{0.1}B_{0.1}calcium_{0.2}P_{0.1}Si_{0.6}O_{2.95}C-15

SnAl_{0.4}B_{0.2}Mg_{0.1}Si_{0.6}O_{3.2}C-16 SnAl_{0.1}B_{0.3}P_{0.1}Si_{0.5}O_{3.05}C-17 SnB_{0.1}K_{0.5}P_{0.1}SiO_{3.65}C-18

SnB_{0.5}F_{0.1}Mg_{0.1}P_{0.5}O_{3.05}[0134] Although any method of the calcinating method and a solution method can be used for the amorphous oxide in this invention, and/or a cull scorch night, its calcinating method is more desirable. After often mixing the oxide, cull scorch night, or compound of the element which corresponds, respectively by the calcinating method, it is desirable to calcinate and to obtain an amorphous oxide and/or a cull scorch night. These are already producible by the well-known method.

[0135] The average grain size of the negative-electrode material used for this invention has desirable 0.1-60 micrometers. In order to make it a predetermined grain size, the grinder and classifier which were known well are used. For example, a mortar, a ball mill, a sand mill, a vibration ball mill, a satellite ball mill, a planet ball mill, a revolution air current type jet mill, a screen, etc. are used. At the time of pulverization, wet grinding which made organic solvents, such as water or a methanol, live together can also be performed if needed. It is desirable to perform a classification in order to consider as a desired particle size. As the classification method, there is especially no limitation and it can use a screen, a pneumatic elutriation machine, etc. if needed. A classification can use dry type and wet.

[0136] In this invention, the metal in which occlusion, the carbon material which can be emitted, a lithium and a lithium alloy, and a lithium and an alloy are possible is mentioned in a lithium ion or a lithium metal as a negative-electrode material which can be combined and can be used for the amorphous oxide negative-electrode material consisting mainly of Sn, Si, and germanium.

[0137] the electrode used for this invention -- the non-proton nature organic solvent else [, such as an electric conduction agent, a binder, and a filler,] is added by the mixture

[0138] In the constituted cell, if the aforementioned electric conduction agent is an electronic-conduction nature material which does not cause a chemical change, it is good anything. Usually, conductive material, such as natural graphites (a flaky graphite, a scale-like graphite, earthy graphite, etc.), an artificial graphite, carbon black, acetylene black, KETCHIEN black, a carbon fiber, and metal powders (copper, nickel, aluminum, silver (JP,63-148554,A), etc.), a metal fiber or a polyphenylene derivative (JP,59-20971,A), can be included as one sort or such mixture. Especially

combined use of a graphite and acetylene black is desirable. The addition has desirable 1 - 30 mass %, and its 2 - 30 mass % is especially desirable. In carbon or especially a graphite, 2 - 15 mass % is desirable.

[0139] this invention -- an electrode -- the binder for holding a mixture can be used As an example of a binder, the polymer which has polysaccharide, thermoplastics, and rubber elasticity is mentioned. As a desirable binder, starch, a carboxymethyl cellulose, A cellulose, a diacetyl cellulose, a methyl cellulose, a hydroxyethyl cellulose, Hydroxypropylcellulose, alginic-acid Na, a polyacrylic acid, Polyacrylic-acid Na, a polyvinyl phenol, a polyvinyl methyl ether, Polyvinyl alcohol, a polyvinyl pyrrolidone, a polyacrylonitrile, Water-soluble polymer, such as a polyacrylamide, PORIHIDOROKISHI (meta) acrylate, and a styrene-maleic-acid copolymer, Polyvinyl chloride, a polytetrafluoroethylene, a polyvinylidene fluoride, A tetrapod FURORO ethylene-hexa FURORO propylene copolymer, a vinylidene fluoride-tetrapod FURORO ethylene-hexa FURORO propylene copolymer, Polyethylene, polypropylene, an ethylene-propylene-diene terpolymer (EPDM), Sulfonation EPDM, a polyvinyl-acetal resin, a methylmetaacrylate, The acrylic-ester (meta) copolymer containing acrylic esters (meta), such as 2-ethylhexyl acrylate The polyvinyl ester copolymer containing vinyl esters, such as an acrylic-ester-acrylonitrile copolymer and vinyl acetate, (Meta) A styrene-butadiene copolymer, an acrylonitrile-butadiene copolymer, A polybutadiene, neoprene rubber, a fluororubber, a polyethylene oxide, An emulsion (latex) or suspensions, such as a polyester polyurethane resin, a polyether polyurethane resin, a polycarbonate polyurethane resin, polyester resin, phenol resin, and an epoxy resin, can be mentioned. The latex of a polyacrylic ester system, a carboxymethyl cellulose, polytetrafluoroethylene, and a polyvinylidene fluoride are mentioned especially preferably. these binders are independent -- or it can mix and use if there are few additions of a binder -- an electrode -- the holding power and cohesive force of a mixture are weak If many [too], electrode volume will increase and an electrode unit volume or the capacity per unit mass will decrease. The addition of a binder has desirable 1 - 30 mass % at such a reason, and 2 - 10 mass % is especially desirable.

[0140] In the constituted cell, the aforementioned filler can be used anything, if it is the fibrous material which does not cause a chemical change. Usually, fiber, such as olefin system polymer, such as polypropylene and polyethylene, glass, and carbon, is used. Although especially the addition of a filler is not limited, 0 - 30 mass % is desirable.

[0141] The electrolyte constituent of this invention can be used for safety reservation, using together with a separator. The separator used together for safety reservation needs to have the function which blockades the above-mentioned crevice above 80 degrees C, raises resistance, and intercepts current, and it is desirable that lock out temperature is 90 degrees C or more 180 degrees C or less.

[0142] The configurations of the hole of a separator are usually a round shape and an ellipse form, a size is 0.05-30 micrometers and its 0.1-20 micrometers are desirable. You may be the hole of the shape of a rod, or an indeterminate form like [at the time of furthermore making by the extending method and the phase separation method]. It is 20 - 90%, the ratio, i.e., the porosity, which these crevices occupy, and it is desirable. [35 - 80% of]

[0143] Even if these separators are single material, such as polyethylene and polypropylene, they may be two or more sorts of composite-sized material. Especially the thing that carried out the laminating of two or more sorts of fine porosity films into which an aperture, porosity, the lock out temperature of a hole, etc. were changed especially is desirable.

[0144] The electronic-conduction object which does not cause a chemical change in the constituted cell as a charge collector of positive and a negative electrode is used. As a charge collector of a positive electrode, aluminum and an aluminium alloy have the desirable especially desirable thing which made the front face of aluminum or stainless steel else [, such as aluminum, stainless steel, nickel and titanium,] process carbon, nickel, titanium, or silver. As a charge collector of a negative electrode, copper and a copper alloy have desirable especially desirable copper, stainless steel, nickel, and titanium.

[0145] Although a film sheet-like thing is usually used, what was netted and punched, a lath object, a porosity object, a foam, the Plastic solid of a fiber group, etc. can be used for the configuration of a charge collector. Although especially thickness is not limited, it is 1-500 micrometers. Moreover, as

for a current collection body surface, it is also desirable to attach irregularly with surface treatment.

[0146] The configuration of a cell can apply a sheet, an angle, a cylinder, etc. to all. On a charge collector, the mixture of a positive active material or negative-electrode material is applied, (coat) dried and compressed, and is mainly used. As the method of application, the reverse rolling method, the direct rolling method, the blade method, the knife method, the extrusion method, the curtain method, the gravure method, the bar method, the dipping method, and the squeeze method can be mentioned, for example. The blade method, the knife method, and the extrusion method are desirable also in it. As for an application, it is desirable to carry out the speed for 0.1-100m/. Under the present circumstances, according to the solution physical properties of a mixture, and a drying property, the surface state of a good application layer can be obtained by selecting the above-mentioned method of application. The time of one side [every] ** or double-sided **** is sufficient as an application.

[0147] Moreover, continuation, intermittence, or a stripe is sufficient as an application. Although the thickness, length, and width of the application layer are decided with the configuration and size of a cell, the thickness of the application layer of one side is in the state where it was compressed after dry, and its 1-2000 micrometers are desirable.

[0148] Dryness of an electrode sheet application object and the dehydration method can carry out the thing of hot blast, a vacuum, infrared radiation, far infrared rays, an electron ray, and the damp wind using independent or the combined method. The range of drying temperature of 80-350 degrees C is desirable, and its range which is 100-250 degrees C is especially desirable. moisture content -- the cell whole -- 2000 ppm or less -- desirable -- a positive electrode -- a mixture and a negative electrode -- it is desirable to make it 500 ppm or less in a mixture or an electrolyte, respectively Although the method generally adopted can be used for the method of pressing a sheet, especially its calender pressing method is desirable. Although especially press ** is not limited, its 0.2 - 3 t/cm2 is desirable. The press speed of the calender pressing method has the amount of desirable 0.1-50m/, and press temperature has desirable room temperature -200 degree C. As for the ratio of negative-electrode sheet width of face to a positive-electrode sheet, 0.9-1.1 are desirable, and 0.95-especially 1.0 are desirable. the content ratio of a positive active material and negative-electrode material -- a compound kind and a mixture -- it changes with prescription

[0149] After processing it into a sheet-like cell as it is after piling up a positive and negative electrode sheet through a separator, or bending, it inserts in a square shape can, and after connecting a sheet with a can electrically, the electrolyte constituent of this invention is poured in and a square shape cell is formed using an obturation board. Moreover, after inserting in a cylinder-like can after piling up and rolling a positive and negative electrode sheet through a separator, and connecting a sheet with a can electrically, the electrolyte constituent of this invention is poured in and a cylinder cell is formed using an obturation board. At this time, a relief valve can be used as an obturation board. It may be equipped with the various safe elements known from the former besides a relief valve. For example, a fuse, bimetal, a PTC element, etc. are used as an overcurrent-protection element.

[0150] Moreover, the method of making a cut in a cell can, the gasket crack method, the obturation board crack method, or cutting process with a lead board can be used for everything but a relief valve as a cure of an internal pressure rise of a cell can. Moreover, the protection network which built the surcharge and the cure against an overdischarge into the battery charger may be made to provide, or you may make it connect independently.

[0151] Moreover, the method which intercepts current by the rise of cell internal pressure can be provided as a cure against overcharge. At this time, the compound which raises internal pressure can be included in a mixture or an electrolyte. as the example of the compound used in order to raise internal pressure -- Li2 -- carbonates, such as CO3, LiHCO3, Na2CO3, and NaHCO3, CaCO3, MgCO3, etc. can be mentioned

[0152] A metal and an alloy with electrical conductivity can be used for a can or a lead board. For example, metals or those alloys, such as iron, nickel, titanium, chromium, molybdenum, copper, and aluminum, are used.

[0153] A well-known method (for example, electric welding of a direct current or an alternating current, laser welding, ultrasonic welding) can be used for the welding process of a cap, a can, a sheet, and a lead board. The compound and mixture which are known from the former, such as

asphalt, can be used for the sealing compound for obturation.

[0154] Although especially the use of the non-water rechargeable battery of this invention is not limited, when it carries in electronic equipment, for example, A notebook computer, pen input personal computer, mobile personal computer, and Electronic Book player, a cellular phone and a cordless phon -- a cordless handset, a pager, and a handy terminal -- Pocket facsimile, a pocket copy, a pocket printer, a headphone stereo, A video movie, a liquid crystal television, a handy cleaner, portable CD, a mini disc, an electric shaver, a transceiver, an electronic notebook, a calculator, memory card, a pocket tape recorder, radio, a backup power supply, memory card, etc. are mentioned. In addition, as a noncommercial use, an automobile, electric vehicles, a motor, lighting fitting, a toy, a game machine machine, a load conditioner, a clock, a stroboscope, a camera, medical equipment (a pacemaker, a hearing-aid, shoulder Japanese fir machine, etc.), etc. are mentioned. Furthermore, it can use as the various objects for munitions, and an object for space. Moreover, it is also combinable with a solar battery.

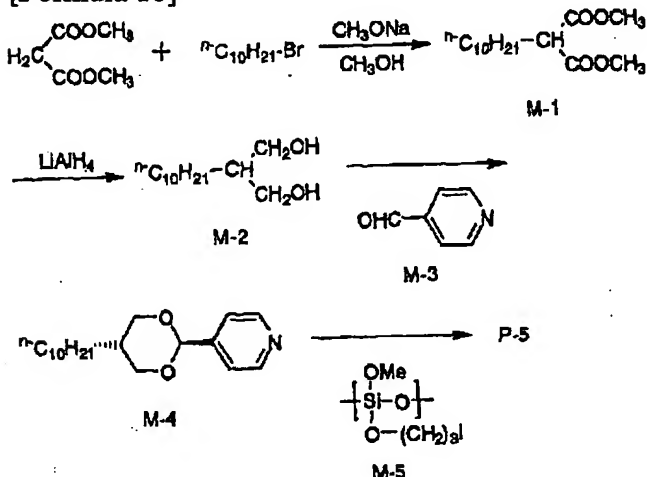
[0155]

[Example] Hereafter, an example explains this invention concretely.

- The instantiation compound P-5 was compounded by the synthetic example-following composition scheme of the instantiation compound P-5.

[0156]

[Formula 18]



[0157] ** The synthetic dimethyl malonate of intermediate field M-1; after dissolving 58.1g (439mmol) in the methanol, adding methanol 28% solution; 88ml of a sodium methoxide and dropping 1-BUROMO decane 97.2g (439mmol) over 1 hour, it flowed back for 8 hours. Diluted hydrochloric acid was filled with reaction mixture, and ethyl acetate extracted after neutralization. Vacuum concentration of the extraction solution was carried out after dryness with magnesium sulfate, vacuum distillation of the residue was carried out, and M-1 [41g (fraction (399Pa (3mmHg) / 82 degrees C))] was obtained.

[0158] ** The solution which was obtained by the above-mentioned ** and which dissolved M-1 (41g, 170mmol) in diethylether (50ml) was dropped over 2 hours, having distributed the synthetic lithium aluminum hydride (11g, 289mmol) of intermediate field M-2 to 150ml diethylether, and stirring at a room temperature. After dropping, after flowing back for 3 hours, diluted hydrochloric acid/ice was slowly filled with reaction mixture, and it extracted, after making a solution acid. The bottom solvent of reduced pressure was distilled off for the extract after dryness with magnesium sulfate, and the oily matter of 31g of rough products was obtained. The rough product was refined in silica gel column chromatography, and 14g was obtained as M-2 and colorless oily matter.

[0159] ** M-2 (13.85g, 64mmol) obtained by the synthetic above of intermediate field M-4 and M-3 (6.86g, 64mmol) were distributed in toluene (50ml). Para-toluenesulfonic acid (12g) was added, and

(0.80g, 0.04mmol) were distributed in toluene (50ml), Para toluenesulfonic acid (12g) was added, and heating reflux was carried out for 5 hours, distilling off water. The water (100ml) which added potassium carbonate (10g) was filled with reaction mixture, ethyl acetate extracted, and the solvent was distilled off under reduced pressure after drying an extract. The residue was recrystallized in the acetonitrile, and M-4 of the purpose was considered as the crystal, and was obtained 7g.

[0160] ** It distributed to the acetonitrile (50ml) and the dimethylacetamide (20ml), and M-4 (5g, 16.4mmol) and polymer M-5 (3g) which were obtained by the synthetic above of P-5 were made to react at 80 degrees C for 10 hours. The solvent was distilled out of reaction mixture at 120 degrees C under reduced pressure, and P-5 (7.5g) which has the mesomorphism side chain which is the specified substance was obtained.

[0161] (Example 1)

- With 15g [of titanium dioxides] (Japanese Aerosil Degussa P-25), 45g, 1g (Aldrich make, Triton X-100), and a diameter of 0.5mm zirconia-beads (Nikkato Corp. make) 30g was put into the vessel made from stainless steel of 200ml of content volume which carried out Teflon (registered trademark) coating of the manufacture inside of photoelectrochemical-cell-1-1. titanium-dioxide dispersion liquid, and it distributed in 1500rpm for 2 hours using the Sand-grinder mill (product made from eye MEKKUSU) Zirconia beads were filtered and removed from the distributed object. The mean particle diameter of the titanium dioxide in this case was 2.5 micrometers. The particle size at this time is measured in the master sizer made from MALVERN.

[0162] 1-2. The glass rod was used and the above-mentioned dispersion liquid were applied to the electric conduction side side of the electrically conductive glass (what carried out cutting processing of the Asahi Glass TCO glass-U at the 20mmx20mm size) which coated the tin oxide which doped the production fluorine of TiO₂ electrode (electrode A) which adsorbed coloring matter. Under the present circumstances, the adhesive tape was stretched to the part by the side of an electric conduction side (from an edge to 3mm), and it considered as the spacer, and glass was put in order and it applied eight sheets at a time at once so that an adhesive tape might come to ends. After the application, it exfoliated and the adhesive tape was air-dried for one day at the room temperature. Next, this glass was put into the electric furnace (muffle furnace FP-32 type made from the Yamato science), and it calcinated for 30 minutes at 450 degrees C. It flooded with the ethanol solution (3xten - four mols/(l.)) of coloring matter R-1 for 3 hours, after taking out this glass and cooling. After being immersed in a 4-tert-butyl pyridine for 15 minutes, the air drying of the glass which coloring matter dyed was washed and carried out by ethanol. Thus, the thickness of the photosensitive layer obtained is 10 micrometers, and the coverage of a semiconductor particle was taken as 20 g/m². In addition, the surface electrical resistance of electrically conductive glass was about 30ohm/**.

[0163] 1-3. The acetonitrile was distilled off, applying the acetonitrile solution (an acetonitrile being a constituent and a homogeneous amount) of the electrolyte constituent (E-102 to E-113) containing Table 1 therefore the adjusted aforementioned specific liquid crystal compound, or a comparison compound to the TiO₂ electrode substrate (1cmx1cm) which is the production **** of a photoelectrochemical cell, and was made and produced and by which the color sensitizing was carried out, and infiltrating it into TiO₂ electrode under 60 degrees C and reduced pressure. The platinum vacuum evaporation glass of the same size was laid on top of these electrodes, and the photoelectrochemical cell (sample B-102-113) was obtained. Moreover, after laying the electrolytic solution (E-101 of Table 1) using the solvent on top of the same TiO₂ electrode substrate (2cmx2cm) as the above by which coloring matter sensitization was carried out with the platinum vacuum evaporation glass of the same size as the electrode, it infiltrated the electrolytic solution into the crevice between both glass using capillarity, and produced the photoelectrochemical cell (sample B-101).

[0164] The photoelectrochemical cell by which the laminating of the platinum layer 6 and glass 7 which serve as electrically conductive glass 1 (that by which the conductive layer 3 was ****(ed) on glass 2), a photosensitive layer 4 (TiO two-layer coloring matter was made to stick to), the electrolyte layer 5, and a counter electrode by this example as shown in drawing 2 was carried out to order was produced.

[0165]

[Table 1]

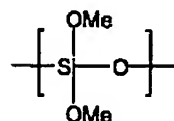
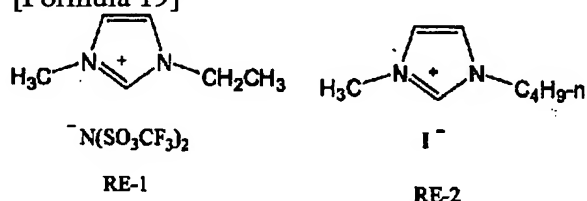
表1 電解質の組成

電解質	組成 (質量%)	サンプル	備考
E-101	(C ₄ H ₉) ₄ N ⁺ I ⁻ (48)/BCE(50)/I ₂ (2)	B-101	比較
E-102	(C ₄ H ₉) ₄ N ⁺ I ⁻ (48)/RE-1(50)/I ₂ (2)	B-102	比較
E-103	RE-2(48)/RE-1(50)/I ₂ (2)	B-103	比較
E-104	(C ₄ H ₉) ₄ N ⁺ I ⁻ (48)/RE-3(50)/I ₂ (2)	B-104	比較
E-105	P-5 (98) /I ₂ (2)	B-105	本発明
E-106	P-8 (98) /I ₂ (2)	B-106	本発明
E-107	P-11 (98) /I ₂ (2)	B-107	本発明
E-108	P-14 (98) /I ₂ (2)	B-108	本発明
E-109	P-5 (48) /P-6(50)/I ₂ (2)	B-109	本発明
E-110	P-8 (48) /P-9(50)/I ₂ (2)	B-110	本発明
E-111	P-8 (48) /P-10(50)/I ₂ (2)	B-111	本発明
E-112	P-11 (48) /P-12(50)/I ₂ (2)	B-112	本発明
E-113	P-11 (48) /P-13(50)/I ₂ (2)	B-113	本発明

BCE (溶媒) : ビスシアノエチルエーテル

[0166]

[Formula 19]



[0167] 1-4. By letting AM1.5 filter (product made from Oriel), and a sharp cut filter (KenkoL-41) pass for the light of the xenon lamp of measurement 500W of a photoelectric conversion efficiency (USHIO make), the simulation sunlight which does not include ultraviolet rays was generated and this luminous intensity was adjusted to 100 mW/cm².

[0168] The electrical and electric equipment which connected the crocodile clip, respectively, irradiated simulation sunlight at 70 degrees C, and was generated on the above-mentioned electrically conductive glass and above-mentioned platinum vacuum evaporation glass of a photoelectrochemical cell was measured in the current-potential measuring device (case the SMU238 type). the open circuit voltage (Voc) of the photoelectrochemical cell called for by this, short-circuit current density (Jsc), and a form factor -- (FF) [= maximum output/(open-circuit-voltage x short-circuit current)] and a conversion efficiency (eta), and constant temperature -- the decreasing rate of the short-circuit current density after carrying out the passage of time for 400 hours was collectively indicated to Table 2 under constant humidity (60 degrees C, 70%R.H.)

[0169]

[Table 2]

表2 光電変換性能

サンプル	Jsc (mA/m ²)	Voc (V)	FF	η (%)	Jsc低下率(%) 80℃-湿度70% 400時間	備考
B-101	11.0	0.60	0.55	4.4	0.0	比較

B-101	11.3	0.60	0.63	4.4	57	比較
B-102	8.1	0.56	0.54	2.4	45	比較
B-103	8.5	0.54	0.56	2.6	23	比較
B-104	8.9	0.57	0.57	3.0	10	比較
B-105	10.4	0.66	0.67	4.5	3	本発明
B-106	10.3	0.66	0.68	4.3	4	本発明
B-107	10.5	0.67	0.66	4.6	3	本発明
B-108	10.6	0.67	0.65	4.6	5	本発明
B-109	11	0.62	0.64	4.3	6	本発明
B-110	11	0.63	0.65	4.5	6	本発明
B-111	11.1	0.63	0.63	4.4	5	本発明
B-112	10.7	0.65	0.64	4.5	5	本発明
B-113	10.5	0.65	0.64	4.3	4	本発明

Jsc : 短絡電流密度、Voc : 開放電圧、FF : 形状因子、 η : 変換効率

[0170] From the above-mentioned result, since a solvent volatilizes, the photoelectrochemical cell (B-101) using the solvent as the electrolytic solution is understood that endurance is very bad. Moreover, by passing, although the cell (B-104) using polysiloxane RE-3 which do not have fused salt RE-1, the cell (B-102, B-103) using RE-2, and mesomorphism substituent of a comparison compound is small, it understands that a photo-electric-translation performance is not enough for degradation in the time. The photoelectrochemical cell using the electrolyte constituent containing the aforementioned specific liquid crystal compound is excellent in initial performances, such as short-circuit current density and a conversion efficiency, and endurance to them. Such an effect was seen when which coloring matter was used.

[0171] (Example 2)

- As a Production Positive Active Material of Lithium Rechargeable Battery-2-1. Positive-Electrode Sheet LiCoO₂ 43 weight sections, the scale-like graphite 2 weight section, the acetylene black 2 weight section, Furthermore, add the polyacrylonitrile 3 weight section as a binder, and the slurry which kneaded the acrylonitrile 100 weight section as a medium, and was obtained is painted on an aluminum foil with a thickness of 20 micrometers using an extrusion formula application machine. After pressing with the calender press machine after dryness, the lead board made from aluminum was welded to the edge, and the positive-electrode sheet with 95 micrometers [in thickness] and a width-of-face [of 54mm] x length of 49mm was produced.

[0172] 2-2. as the production negative-electrode active material of a negative-electrode sheet -- a meso face pitch system carbon material (PETOKA) -- as 43 weight sections and an electric conduction agent -- the acetylene black 2 weight section and the graphite 2 weight section -- comparatively -- coming out -- mixing -- further -- as a binder -- a polyacrylonitrile -- 3 weight sections -- adding -- the N-methyl pyrrolidone 100 weight section -- as a medium -- kneading -- a negative electrode -- a mixture -- the slurry was obtained a negative electrode -- a mixture -- the slurry was painted on copper foil with a thickness of 10 micrometers using the extrusion formula application machine, it pressed with the calender press machine after dryness, and the negative-electrode sheet with 46 micrometers [in thickness] and a width-of-face [of 55mm] x length of 50mm was produced After welding the lead board made from nickel to the edge of a negative-electrode sheet, it heat-treated at 230 degrees C for 1 hour in dry air of -40 degrees C or less of dew-points. Heat treatment was performed using the far-infrared heater.

[0173] The production negative-electrode sheet of a 2-3. sheet cell and the positive-electrode sheet carried out dehydration dryness at 230 degrees C for 30 minutes in dry air of -40 degrees C or less of dew-points, respectively. In dry atmosphere, the laminating of the separator (polyethylene porosity film) and nonwoven fabric which were judged in a dried [dehydration] positive-electrode sheet with a width-of-face [of 54mm] x length of 49mm and width-of-face [of 60mm] x length of 60mm was carried out, the liquid which dissolved the electrolyte (E-202-213) of composition adjusted according to Table 3 on the nonwoven fabric in the acetonitrile of the amount of said was applied, and the acetonitrile was distilled off under reduced pressure at 50 degrees C. Moreover, the electrolytic solution (E-201) using the solvent was infiltrated into the nonwoven fabric as it is. The laminating of the dried [dehydration] negative-electrode sheet with a width-of-face [of 55mm] x length of 50mm was carried out on it, using the sheathing material which consists of a laminate film of a polyethylene (50 micrometers)-polyethylene terephthalate (50 micrometers), heat weld was carried out, four edges

were sealed under the vacuum, and the sheet type cell (sample B-201-213) was produced.

[0174] The sheet type cell by which the laminating of the positive-electrode sheet 31 equipped with the negative-electrode sheet 33 equipped with the negative-electrode terminal 35, the solid polymer electrolyte 32, and the positive-electrode terminal 34 by this example as shown in drawing 3 was carried out to order was produced.

[0175]

[Table 3]

表3 電解質の組成

電解質番号	電解質組成 (質量%)	電池番号	備考
E-201	RE-4(30)/PC(30)/EC(40)	B-201	比較
E-202	RE-4(30)/RE-1(70)	B-202	比較
E-203	RE-4(30)/PG1000	B-203	比較
E-204	LiClO ₄ (30)/RE-3(70)	B-204	比較
E-205	P-17(100)	B-205	本発明
E-206	P-19(100)	B-206	本発明
E-207	P-21(100)	B-207	本発明
E-208	P-22(100)	B-208	本発明
E-209	P-17(50)/P-18(50)	B-209	本発明
E-210	P-19(50)/P-20(50)	B-210	本発明
E-211	RE-3(30)/ P-18(70)	B-211	本発明
E-212	RE-3(30)/ P-20(70)	B-212	本発明
E-213	LiBF ₄ (30)/P-23(70)	B-213	本発明

RE-4 : LiN(SO₂CF₃)₂

PC : プロピレンカーボネート

EC : エチレンカーボネート

PG1000 : ポリエチレングリコール (平均分子量 1000)

[0176] 2-4. About the sheet type cell produced by the method of the evaluation above of a cell performance, charge and discharge were repeated 30 times on condition that current density 1.3 mA/cm², charge final-voltage 4.2V, and discharge-final-voltage 2.6V**, and the service capacity in 30 cycle eye was calculated. This was investigated about five cells of the same prescription, and the average was made into the capacity of the cell. Thus, the capacity of each cell was calculated and the relative capacitor to a sample B-201 was calculated. Moreover, the service capacity of the 200 cycle eye of each cell was calculated, the ratio to the service capacity of 10 cycle eye was calculated, and it expressed as a cycle capacity. Each value was shown in Table 4.

[0177]

[Table 4]

表4 電池性能

電池番号	相対容量	サイクル容量	備考
B-201	1	0.30	比較
B-202	0.59	0.91	比較
B-203	0.31	0.77	比較
B-204	0.70	0.91	比較
B-205	0.88	0.95	本発明
B-206	0.87	0.95	本発明
B-207	0.85	0.96	本発明
B-208	0.86	0.98	本発明
B-209	0.95	0.95	本発明
B-210	0.94	0.94	本発明
B-211	0.96	0.94	本発明
B-212	0.98	0.93	本発明
B-213	0.96	0.94	本発明

[0178] It turns out that the electrolyte which contains the aforementioned specific liquid crystal compound from the above-mentioned result is raising cycle nature, without seeing the big fall of capacity.

[0179] From these examples, the electrolyte which did not volatilize substantially and was excellent in using the aforementioned specific liquid crystal compound at charge transportability ability was obtained, thereby, it excelled in the photoelectric transfer characteristic and the photoelectrochemical

cell with little property degradation by the passage of time was obtained. Furthermore, this electrolyte does not reduce cell capacity and it turns out that it is the lithium ion conduction material which was moreover excellent in the cycle property.

[0180]

[Effect of the Invention] As mentioned above, according to this invention, the electrolyte constituent excellent in endurance and ion conductivity can be offered, and the electrochemical cell excellent in endurance and the electrical property (photoelectric transfer characteristic) using the electrolyte constituent concerned, a non-water rechargeable battery, and a photoelectrochemical cell can be offered further.

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TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to the electrolyte constituent containing a liquid crystal compound, the electrochemical cell using electrolyte ***** especially a non-water rechargeable battery, and a photoelectrochemical cell further.

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PRIOR ART

[Description of the Prior Art] The electrolyte used for electrochemical cells, such as a non-water rechargeable battery and a coloring matter sensitization solar battery, is a medium which has the function (it is called ionic conduction) to convey the ion to inter-electrode, including the carrier ion according to the purpose. For example, in the lithium secondary battery which is the representation of a non-water rechargeable battery, transportation of a lithium ion does the influence for the performance of an electrochemical cell with the big conductivity of iodine ion and iodine trimer ion in a coloring matter sensitization solar battery. In these cells, generally, although the solvent system with high ion conductivity was used abundantly as an electrolyte, there was a problem of an exhaustion of the solvent at the time of including in a cell and leakage reducing the endurance of a cell. Moreover, in order to seal a solution in a lithium secondary battery and to have to use a metal vessel, it was difficult for cell mass to become heavy and to also give flexibility to a cell configuration. In order to conquer the fault of such a solution system electrolyte, various electrolytes are proposed in recent years. The so-called gel electrolyte (JP,61-23945,B public relations, JP,61-23947,B public relations) which made the solution electrolyte permeate a polymer matrix has not inhibited volatilization of a solvent completely, although the fall of the ionic conductivity to a solution system electrolyte does not drop a cell performance small. Moreover, although the polymer electrolyte (-2184 or KMurata, Electrochimica Acta, Vol.40, No.13-14, and p2177 1995) which dissolved the salt in polymer, such as a polyethylene oxide, is expected as what solves the problem of a solution system electrolyte, ionic conductivity's is not yet enough. On the other hand, although an opposite anion is room temperature fused salt with imidazolium salts and pyridinium salts liquefied at a room temperature, such as BF₄⁻ and 2 (CF₃SO₂)N⁻, and it is proposed as an electrolyte for lithium ion batteries, an electrolytic mechanical strength and ion conductivity conflict, and when own viscosity of fused salt was raised, or it is the means of making polymer contain etc. and a mechanical strength is strengthened, the fall of ionic conductivity is seen. Furthermore, ion conductivity temperature dependence was large and the above electrolytes of especially the ion conductivity in low temperature were inadequate.

[0003] By the way, although compound solar batteries, such as a single-crystal-silicon solar battery, a polycrystal silicon solar cell, an amorphous-silicon solar cell, a cadmium telluride, and selenium-ized indium copper, are set as the object of utilization or research and development, the photovoltaics which transform a light energy into electrical energy need to conquer troubles, such as reservation of a manufacturing cost and raw material, and the length of an energy pay back time, when making it spread. On the other hand, although many solar batteries using the organic material which pointed to large-area-izing or low-pricing were also proposed until now, the conversion efficiency was low and there was a problem that endurance was also bad.

[0004] In such a situation, the technology of a photoelectrochemical cell using the optoelectric transducer (it abbreviates to a coloring matter sensitization optoelectric transducer henceforth) using the oxide semiconductor by which sensitization was carried out to Nature (the 353rd volume, the 737-740th page, 1991), U.S. JP,4927721,B, etc. with coloring matter, and this was indicated. This cell consists of the optoelectric transducer, charge transfer layer, and counter electrode which function as a negative electrode. An optoelectric transducer consists of a conductive base material and a photosensitive layer, and a photosensitive layer contains the semiconductor with which coloring matter stuck to the front face. A charge transfer layer consists of a oxidation reduction object, and

bears charge transportation between a negative electrode and a counter electrode (positive electrode). In the photoelectrochemical cell proposed by the above-mentioned patent, the solution (electrolytic solution) which uses salts, such as potassium iodide, as an electrolyte as a charge transfer layer was used. This method was cheap and it was a problem for a photoelectric conversion efficiency not to fall remarkably by evapotranspiration of the electrolytic solution and exhaustion, if it is used over a long period of time, although it is promising, or to stop functioning as a cell in that a comparatively high energy conversion efficiency (photoelectric conversion efficiency) is obtained.

[0005] The method of using as an electrolyte the imidazolium salt which is a low melting point compound as the exhaustion prevention method of the electrolytic solution at WO 95/No. 18456 is indicated to this problem. Since according to this method water and the organic solvent which were used as an electrolytic solvent were unnecessary or little and ended conventionally, although the improvement of endurance was found, still, when endurance is inadequate and the imidazolium salt was made into high concentration, while viscosity became high, charge transportation ability fell, and there was a problem that a photoelectric conversion efficiency became low. Furthermore, there is the method of using a thoria ZORIUMU salt as an electrolyte, and the same problem as an imidazolium salt arises also in this method.

[0006] As mentioned above, it is a very difficult technical problem that it is compatible in a mechanical strength and ion conductivity as an electrolyte of electrochemical cells, such as a lithium ion rechargeable battery and a solar battery.

[0007] As one method of solving these, making an electrolyte constituent contain a mesomorphism compound is proposed. The part which has the coordination ability to ion, such as an alkyleneoxy machine, as these examples, and the compound which has a meso gene machine (JP,11-86629,A), The compound (JP,4-323260,A) with which the meso gene machine was introduced into the polyethylene-oxide chain, the compound (JP,11-116792,A) which has a mesomorphism part in the side chain of a polyethylene oxide, the compound (JP,6-19923,B) with which the meso gene machine was introduced into the side chain of a polysiloxane through the oligo oxyethylene spacer are shown. These consist of a motile flexible high part which dissolves an electrolyte salt and conducts ion by carrying out complexing to a cation, and an upright part (meso gene machine) for carrying out molecular association, in order to maintain a mechanical strength.

[0008] By the way, in order for an electrolyte to function efficiently in an electrochemical cell from Shigehara's and others latest research (Journal of Power Source, 92 volumes, 120 - 123 pages, 2001), it turns out besides ionic conductivity being high that it conducts more nearly alternatively [carrier ion], i.e., it is a performance overlay important point that the carrier ion transference number is high. For example, in a lithium ion battery, it is desirable for the iodine anion transference number to be high in the coloring matter sensitization solar battery from which the lithium ion transference number's being high and an iodine anion serve as a carrier. In the mesomorphism compound mentioned above, the strong basis of cations, such as a polyalkylene oxide, and an interaction restricted the cation, and has caused decline in the cation transference number. Moreover, since molecular-motion nature falls, the improvement in the ionic conductivity itself is not expectable with complexing with a cation, either.

[0009] The oligo oxyethylene part which the polysiloxane by which alkylation was carried out to the electrolyte constituent which introduced the meso gene machine into the side chain of the polysiloxane which shows **** and is indicated by Japanese Patent Publication No. [like] No. 19923 [six to] on the other hand is illustrated, and, as for this electrolyte constituent, restricts a cation strongly serves as a medium of ionic conduction, and is the expectable [the high cation transference number] present condition.

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EFFECT OF THE INVENTION

[Effect of the Invention] As mentioned above, according to this invention, the electrolyte constituent excellent in endurance and ion conductivity can be offered, and the electrochemical cell excellent in endurance and the electrical property (photoelectric transfer characteristic) using the electrolyte constituent concerned, a non-water rechargeable battery, and a photoelectrochemical cell can be offered further.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] this invention solves many problems in the aforementioned former, and makes it a technical problem to attain the following purposes. That is, the first purpose of this invention is offering the electrolyte constituent excellent in endurance and ion conductivity. Furthermore, the second purpose of this invention is offering the electrochemical cell excellent in endurance and the electrical property (photoelectric transfer characteristic) which used the electrolyte constituent concerned, a non-water rechargeable battery, and a photoelectrochemical cell.

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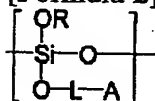
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3. In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] The above-mentioned technical problem is solved by the following means. That is, this invention is an electrolyte constituent containing the liquid crystal compound which repeats the polysiloxane structure shown by the <1> following general formula (I), and it has as a unit.

[0012]

[Formula 2]



一般式 (I)

[0013] R expresses an alkyl group among [general formula (I), and L expresses single bond or a divalent connection machine. A expresses a mesomorphism substituent. However, a mesomorphism substituent may have an ionicity basis and a mesomorphism substituent contains the counter ion in that case.]

[0014] The electrolyte constituent of the aforementioned <1> publication characterized by the mesomorphism substituent which A in the <2> aforementioned general formula (I) expresses being the salt which consists of an anion part containing a meso gene machine, and a cation part which consists of the opposite cation.

An electrolyte constituent given in the above <2> whose <3> aforementioned pairs cation is characterized by being alkali-metal ion.

The electrolyte constituent of the aforementioned <1> publication characterized by the mesomorphism substituent which A in the <4> aforementioned general formula (I) expresses being the salt which consists of a cation part containing a meso gene machine, and an anion part which consists of the opposite anion.

An electrolyte constituent given in the above <4> characterized by being chosen from the group which the <5> aforementioned pairs anion becomes from an iodine anion, a sulfonamide and disulfon imide, N-acyl sulfonamide, a carboxylic acid, a sulfonic acid, alcohol, an activity methylene, and the anion that activity methine dissociated.

The electrolyte constituent given [aforementioned] in <1>- <5> characterized by the <6> aforementioned liquid crystal compound being a polymer-liquid-crystal compound obtained by carrying out a polymerization.

[0015] The electrochemical cell characterized by including the electrolyte constituent of a publication in either of <7> aforementioned <1>- <6>.

The charge transporting bed containing an electrolyte constituent given in either of aforementioned <1>- <6> on <8> conductivity base material, the photosensitive layer containing the semiconductor by which sensitization was carried out with coloring matter, and the photoelectrochemical cell characterized by having a counter electrode.

The non-water rechargeable battery characterized by including the electrolyte constituent of a publication in either of <9> aforementioned <1>- <6>.

[0016]

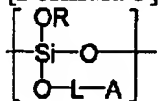
[Embodiments of the Invention] Hereafter, this invention is explained in detail. The electrolyte

constituent of this invention comes to contain the liquid crystal compound which repeats the polysiloxane structure shown by the following general formula (I), and it has as a unit.

[0017] As shown in the following general formula (I), this specific liquid crystal compound repeats the polysiloxane structure by which alkoxy substitution was carried out, and has it as a unit. This polysiloxane structure by which alkoxy substitution was carried out has high maneuverability, and since it can dissolve an electrolyte salt, without restricting a cation strongly, it can realize the cation transference number and ion conductivity higher than an oxyethylene machine. Thus, the polysiloxane structure by which alkoxy substitution was carried out serves as a medium which dissolves an electrolyte salt according to the principal chain, and conducts ion, it is one side, and the part with the upright side chain (mesomorphism substituent) brings about the macroscopic mechanical strength of an electrolyte constituent, without carrying out molecular association, and an ionic conduction medium's forming the structure base material which carried out phase separation micro, and reducing the maneuverability of an ionic conduction medium by mesomorphism. For this reason, the electrolyte constituent of this invention containing a specific liquid crystal compound is excellent in endurance and charge transportability ability.

[0018]

[Formula 3]



一般式 (I)

[0019] Carbon atomic numbers (henceforth, more than C) are 1-24 preferably. the inside of a general formula (I), and R -- alkyl group [-- You may be branched-chain, even if it is 1-10 and is a straight chain-like. more -- being desirable (more than C) -- For example, a methyl, ethyl, a propyl, butyl, i-propyl, i-butyl, Pentyl, hexyl, octyl, 2-ethylhexyl, t-octyl, desyl, dodecyl, tetradecyl, 2-hexyl desyl, hexadecyl, octadecyl, cyclohexyl methyl, and octyl cyclohexyl] is expressed. Furthermore, R may have the substituent. as a desirable substituent Carbon atomic numbers (henceforth, more than C) are 1-24 preferably. alkyl group [which may be replaced -- You may be branched-chain, even if it is 1-10 and is a straight chain-like. more -- being desirable (more than C) -- For example, a methyl, ethyl, a propyl, butyl, i-propyl, i-butyl, A pentyl, a hexyl, an octyl, 2-ethylhexyl, t-octyl, A desyl, a dodecyl, tetradecyl, 2-hexyl desyl, hexadecyl, Octadecyl, cyclohexyl methyl, and octyl cyclohexyl], the aryl group (desirable -- more than C [6-24], for example, a phenyl, --) which may be condensing the ring even if it has replaced 4-methylphenyl, 3-cyano phenyl, 2-chlorophenyl, 2-naphthyl, the heterocycle machine that may be condensing the ring even if it has replaced (the nitrogen in a ring may form 4 class at the time of a nitrogen-containing heterocycle machine.) Preferably More than C [2-24], for example, 4-pyridyl, 2-pyridyl, 1-octyl pyridinium-4-IRU, 2-pyrimidyl, 2-imidazolyl, 2-thiazolyl, and alkoxy-group [-- desirable -- more than C [1-24], for example, a methoxy, -- Ethoxy ** butoxy, octyloxy, methoxyethoxy one, methoxy PENTA (ethyloxy), acryloyl oxyethoxy and pentafluoro propoxy] and an acyloxy machine (desirable -- more than C [1-24], for example, acetyloxy, --) benzoyloxy one and an alkoxy carbonyl group (desirable -- more than C [2-24], for example, a methoxycarbonyl, --) Ethoxycarbonyl, a cyano group, a fluoro machine, an alkoxy carbonyl group, a cyano group, and polymerization nature machines (preferably a vinyl group, an acryloyl machine, a methacryloyl machine, a styryl machine, a cinnamic acid residue, etc.) are mentioned.

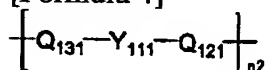
[0020] L expresses single bond or a divalent connection machine among a general formula (I). As an example of a divalent connection machine, -(CH₂)_n- (n shows the integer of 1-15 here), -CH₂CH₂(OCH₂CH₂)_N- (N Shows Integer of 1-10 Here), -CH=CH-, -CH=N-, -N=N-, -N(O)=N-, -COO-, -COS-, CONH-, -COCH₂-, -CH₂NH-, -CO-, -CH=CH-COO-, -CH=CH-CO-, -(C**C)- (N Shows Integer of 1-3 Here), Such Combination, Etc. are Desirable. - (CH₂)_n- (n shows the integer of 3-10 here), -CH₂CH₂(OCH₂CH₂)_n- (n shows the integer of 2-8 here), and such combination are still more desirable.

[0021] Although a mesomorphism substituent is expressed, a meso gene machine is mentioned as a mesomorphism substituent, for example, the inside of a general formula (I) and A are "Flussige

Kristalle in Tabellen II" and Dietrich. Demus and HorstZaschke and the thing of which the 7-18 (1984). publication is done are mentioned. Especially, what is expressed with the following general formula (II) is desirable.

[0022]

[Formula 4]



一般式 (II)

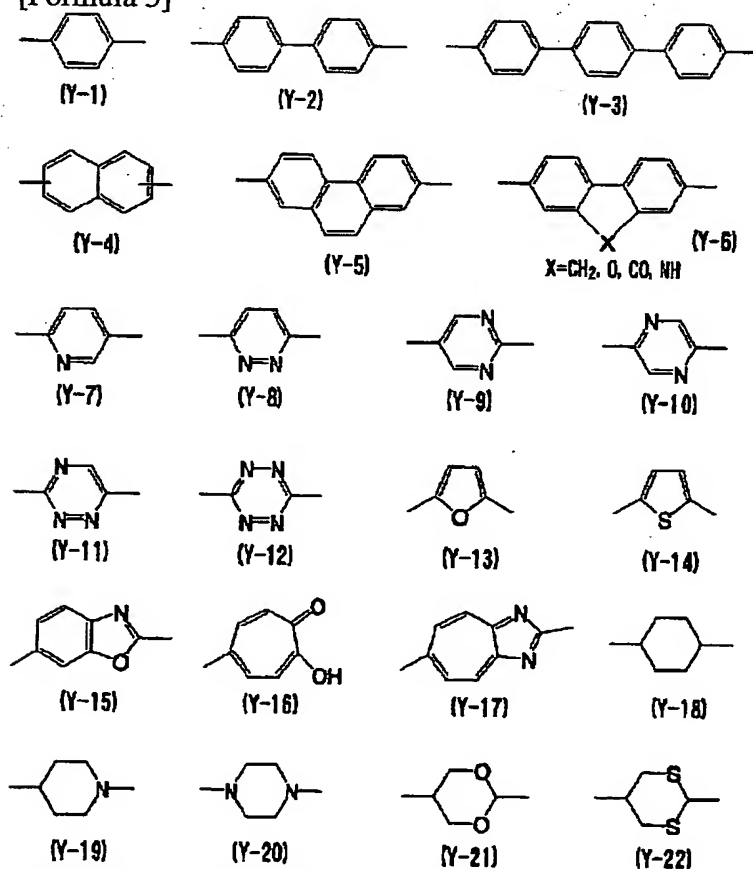
[0023] Y111 expresses the condensed-ring substituent which consists of a divalent 4 or 7 member ring substituent or them among a general formula (II). Q121 and Q131 express a divalent connection machine or divalent single bond, respectively, n2 expresses 1, 2, or 3, and when n2 is 2 or 3, even if two or more Y111, Q121, and Q131 are the same respectively, they may differ.

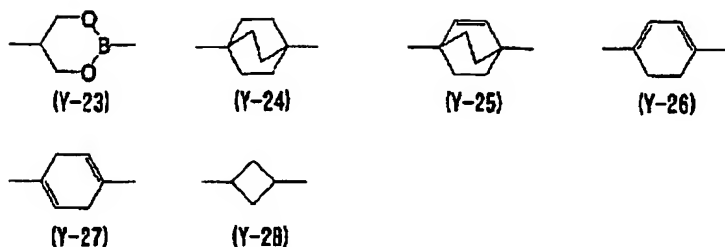
[0024] Q121 and Q131 express a divalent connection machine or divalent single bond among a general formula (II), respectively. As an example of a divalent connection machine, -CH=CH-, -CH=N-, -N=N-, -N(O)=N-, -COO-, -COS-, -CONH-, -COCH2-, -CH2CH2-, -OCH2-, -CH2NH-, -CH2-, -CO-, -O-, -S-, -NH-, -(CH2)1-3-, -CH=CH-COO-, -CH=CH-CO-, -(C**C)1-3-, such combination, etc. are desirable, and -CH2-, -CO-, -O-, -CH=CH-, -CH=N-, -N=N-, and such combination are still more desirable. Moreover, a hydrogen atom may be replaced in these. As for Q121 and Q131, it is desirable that it is especially single bond.

[0025] The inside of a general formula (II), 4, 5, 6 or 7 member ring substituent divalent in Y111, The condensed-ring substituent which consists of them is expressed, and it is still more desirable that they are the saturation of 6 member ring aromatic machine, 4, or 6 member ring or an unsaturation aliphatic machine, 5, 6 member ring heterocycle machines, or those condensed rings. or as these examples Although the following formula (Y-1) - (Y-27) a substituent are mentioned, it is not limited to these. Moreover, you may be such combination. The still more desirable things in these substituents are (Y-1), (Y-2), (Y-18), (Y-19), (Y-21), and (Y-22), and especially desirable things are (Y-1), (Y-2), and (Y-21).

[0026]

[Formula 5]





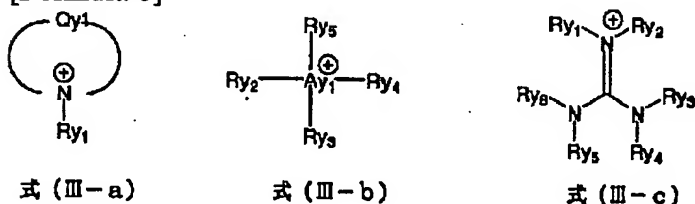
[0027] A mesomorphism substituent may have an ionicity basis and a mesomorphism substituent comes to form the so-called anion part and the so-called cation part, and the salt structure constituted in that case including the counter ion. In case a specific liquid crystal compound adjusts an electrolyte, it can make carrier ion the counter ion of the liquid crystal compound which is ionicity, because this liquid crystal substituent has salt structure. For this reason, since there is no need of adding carrier ion in the form of a salt, separately and mobile ion other than carrier ion is not contained, the transference number of carrier ion can be raised. In this case, the basis which gives mesomorphism as a mesomorphism substituent, for example, a meso gene machine, is contained at least in one side of an anion part and a cation part. The basis which gives mesomorphism may not be included or organic ion (an organic anion, organic cation) or inorganic ion (an inorganic anion, inorganic cation) is sufficient as the anion part or cation part of the direction which has not been directly connected with L in a general formula (I).

[0028] The salt which consists of a salt which consists of an anion part containing a meso gene machine and a cation part which consists of the opposite cation as suitable concrete composition of a mesomorphism substituent or a cation-part containing a meso gene machine, and an anion part which consists of the opposite anion is mentioned. It comes to connect either these anions part and a cation part with L in a general formula (I).

[0029] When a meso gene machine is included in a cation part, structure desirable as the cation part (substituent with a positive charge) is a general formula (III-a) or (III-b) (III-c) structure expressed. As for a meso gene machine, at this time, it is desirable to be contained as a substituent of Ry1-Ry5 in general formula (III-a) - (III-c), or Qy1. Moreover, it is desirable to be contained as the atomic groups Ry1-Ry5 which consist of a repeat unit shown by the aforementioned general formula (I), or a substituent of Qy1.

[0030]

[Formula 6]



[0031] Qy1 of a general formula (III-a) expresses the atomic group which can form the aromatic cation of 5 or 6 member ring with a nitrogen atom, and Ry1 expresses the alkenyl machine which is not replaced [the alkyl group which is not replaced / substitution or /, a polymerization nature machine, substitution, or].

[0032] Ay1 of a general formula (III-b) expresses a nitrogen atom or the Lynn atom, and Ry2, Ry3, Ry4, and Ry5 express respectively the alkenyl machine which is not replaced [the alkyl group which is not replaced / substitution or /, a polymerization nature machine, substitution, or] independently. However, Ry2, Ry3, Ry4, and Ry5 are not aryl groups simultaneous [three or more]. Moreover, two or more of Ry2, Ry3, Ry4, and Ry5 may form the un-aromatic ring which connects mutually and contains Ay1.

[0033] Respectively, independently, Ry1, Ry2, Ry3, Ry4, Ry5, and Ry6 of a general formula (III-c) may express the alkenyl machine which is not replaced [the alkyl group which is not replaced / substitution or /, a polymerization nature machine substitution, or], among those two or more may

connect them mutually, and they may form a ring structure.

[0034] A general formula (III-a), (III-b), and (III-c) the cation expressed may form a polymer through Qy1, or Ry1-Ry6.

[0035] The composition atom of the atomic group Qy1 which can form the cation of aromatic series 5 or 6 member rings with nitrogen is preferably chosen from carbon, hydrogen, nitrogen, oxygen, and sulfur among a general formula (III-a).

[0036] As 6 member rings completed by Qy1, it is a pyridine, a pyrimidine, a pyridazine, a pyrazine, and triazine preferably, and is a pyridine more preferably.

[0037] As a aromatic-series 5 member ring completed by Qy1, it is an oxazole, a thiazole, an imidazole, a pyrazole, an isoxazole, thiadiazole, an OKISA diazole, and a triazole, and they are an oxazole, a thiazole, and an imidazole more preferably. An oxazole and an imidazole are especially desirable.

[0038] A general formula (III-a), and (III-b) (III-c) inner Ry1-inner Ry6 It is the alkyl group (carbon atomic numbers (henceforth, more than C) are 1-24 preferably) which is not replaced [substitution or] independently respectively. Even if it is a straight chain-like, it may be branched-chain, and you may be a ring type. For example, a methyl, ethyl, a propyl, butyl, i-propyl, a pentyl, A hexyl, an octyl, 2-ethylhexyl, t-octyl, a desyl, A dodecyl, tetradecyl, 2-hexyl desyl, octadecyl, cyclohexyl, cyclopentyl and a polymerization nature machine (desirable -- a vinyl group and an acryloyl machine --) Alkenyl machines which are not replaced [substitution or], such as a methacryloyl machine, a styryl machine, and a cinnamic acid residue (more than are 2-24 in C preferably) Even if it is a straight chain-like, it may be branched-chain, for example, a vinyl and an allyl compound are expressed, the alkyl group of more than C 3-18 or the alkenyl machine of more than C 2-18 is expressed preferably, and the alkyl group of more than C 4-6 is expressed more preferably.

[0039] A general formula (III-a), inner Qy1, and Ry1-Ry6 may have the substituent. as an example of a desirable substituent a halogen atom (F, Cl, Br, I), a cyano group, and an alkoxy group (a methoxy -) Ethoxy ** butoxy, octyloxy, methoxyethoxy one, methoxy PENTA (ethyloxy), Aryloxy machines, such as acryloyl oxyethoxy and pentafluoro propoxy one (phenoxy etc.), alkyl thio machines (a methylthio, ethyl thio, etc.) and an acyl group (an acetyl --) sulfonyl machines (a methane sulfonyl --), such as a propionyl and a benzoyl An acyloxies machine, such as benzenesulphonyl (acetoxyl, benzoyloxy, etc.), A sulfonyloxy machine (methane sulfonyloxy, toluenesulfonyloxy, etc.), phosphonyl groups (diethyl phosphonyl etc.) and an amide group (acetyl amino --) carbamoyl groups (N and N-dimethyl carbamoyl --), such as a benzoyl amide alkyl groups (a methyl, ethyl, and a propyl --), such as N-phenylcarbamoyl An isopropyl, a cyclo propyl, butyl, 2-carboxy ethyl, a benzyl, etc., aryl groups (a phenyl, toluyl, etc.) and a heterocycle machine (for example, pyridyl --) Alkenyl machines, such as imidazolyl and furanyl (a vinyl, 1-propenyl, etc.), An alkoxy-group acyloxy machine (acetyloxy, benzoyloxy, etc.), Alkoxy carbonyl groups (a methoxycarbonyl, ethoxycarbonyl, etc.) and polymerization nature machines (preferably a vinyl group, an acryloyl machine, a methacryloyl machine, a styryl machine, a cinnamic acid residue, etc.) are mentioned.

[0040] When a meso gene machine is included in a cation part, as the opposite anion preferably As an inorganic anion, a halogen anion (Cl-, Br-, I-), an iodine trimer anion (I3-), NCS-, BF4-, PF6-, O4Cl-, Ph4B-, AsF6-, SbF6-, and B10Cl10-, It is desirable to be chosen from the group which consists of an anion which a sulfonamide, disulfon imide, N-acyl sulfonamide, a carboxylic acid, a sulfonic acid, alcohol, an activity methylene, and activity methine dissociated as an organic anion. It is chosen from the group which consists of an iodine anion (I-, I3-) and an anion which a sulfonamide, disulfon imide, N-acyl sulfonamide, a carboxylic acid, a sulfonic acid, alcohol, an activity methylene, and activity methine dissociated as an organic anion more preferably. As an iodine anion (I-, I3-) and an organic anion, still more preferably A sulfonic acid, the anion (for example, (CnF2n+1SO2) (CmF2m+1SO2), imido anion expressed with N- (n --)) which disulfo nil imide and N-acyl sulfonamide dissociated m is chosen from the group which consists of six or less positive integer, a fluorosulfonic-acid anion (n is six or less positive integer) expressed with CnF2n+1SO3-, respectively. It is an iodine anion (I-, I3-) especially preferably. This iodine anion is advantageous when using a specific liquid crystal compound as an electrolyte use for solar batteries from which iodine ion serves as a carrier.

[0041] When a meso gene machine is included in an anion part, things desirable as the anion part (substituent with a negative charge) are a sulfonamide, disulfon imide, N-acyl sulfonamide, a carboxylic acid, a sulfonic acid, alcohol, an activity methylene, and the anion in which activity methine carried out proton dissociation.

[0042] When a meso gene machine is included in an anion part, as the above-mentioned general formula (III-a) and (III-b) (III-c) the cation of the structure expressed, and an inorganic cation, a lithium ion is suitably mentioned as an organic cation preferably as the opposite cation. A lithium ion is suitable also especially in these. This lithium ion is advantageous when using a specific liquid crystal compound as a lithium ion battery or an electrolyte for lithium cells.

[0043] It is desirable that an alkyl group or an alkenyl machine is included as a basis which connects with a mesomorphism substituent (the counter ion is also included when it has an ionicity basis) the organic ion which shows an end group or a meso gene machine, and ionicity. As for the carbon number of these alkyl groups or an alkenyl machine, 6 to 25 is desirable, and 6 to 18 is still more desirable. Moreover, you may have the substituent and what was mentioned above as a substituent in R of a general formula (I) as a desirable substituent is mentioned.

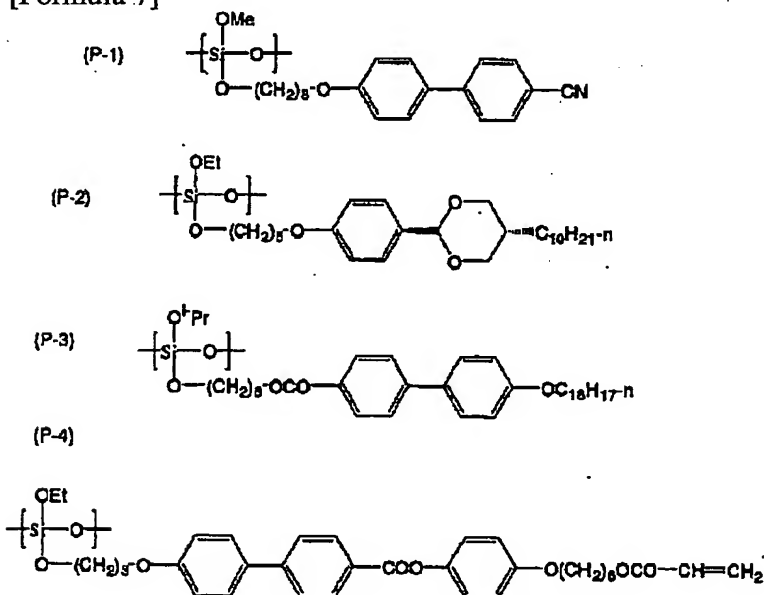
[0044] As a mesomorphism substituent, when using the electrolyte constituent of this invention for a lithium ion battery or a lithium cell use, especially desirable composition is an anion part in which the part connected with L in a general formula (I) contains a meso gene machine, and is the composition that the counter ion used as the cation part is a lithium ion. On the other hand, when using for the solar-battery use from which iodine ion serves as a carrier, it is desirable that it is the composition that the opposite anion which the part connected with L in a general formula (I) is a cation part containing a meso gene machine, and serves as the anion part is iodine ion.

[0045] As a mesomorphism substituent, pKa of the conjugate acid of an anion part is desirable from a viewpoint which raises the dissociation concentration of the ion (for example, a lithium ion, iodine ion, etc.) from which it becomes a carrier in an electrolyte that it is 11 or less, and it is still more desirable that it is seven or less.

[0046] Although the example P-1 to P-28 of the polysiloxane structure shown by the general formula (I) is shown hereafter, this invention is not necessarily limited to these examples. In addition, let the liquid crystal compound which repeats the structure shown by this example and it has as a unit be the instantiation compound P-1 to P-28.

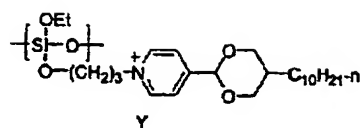
[0047]

[Formula 7]

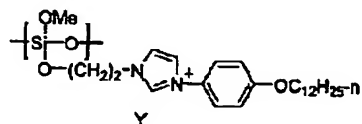


[0048]

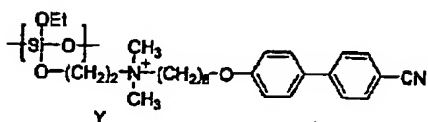
[Formula 8]



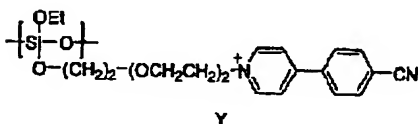
(P-5) $\text{Y} = \text{I}^-$
 (P-6) $\text{Y} = \text{N}(\text{SO}_2\text{CF}_3)_2$
 (P-7) $\text{Y} = \text{CF}_3\text{COO}^-$



(P-8) $\text{Y} = \text{I}^-$
 (P-9) $\text{Y} = \text{N}(\text{SO}_2\text{CF}_3)_2$
 (P-10) $\text{Y} = \text{BF}_4^-$



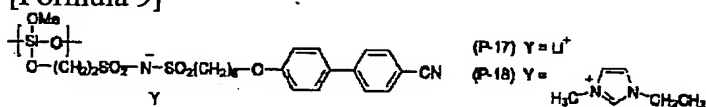
(P-11) $\text{Y} = \text{I}^-$
 (P-12) $\text{Y} = \text{H}_3\text{COOC}-\text{C}^-(\text{SO}_2\text{CF}_3)_2$
 (P-13) $\text{Y} = \text{BF}_4^-$



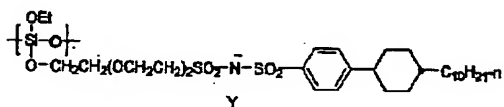
(P-14) $\text{Y} = \text{I}^-$
 (P-15) $\text{Y} = \text{CF}_3\text{CONSO}_2\text{CF}_3$
 (P-16) $\text{Y} = \text{O}(\text{CH}_2)_2\text{CH}_3$

[0049]

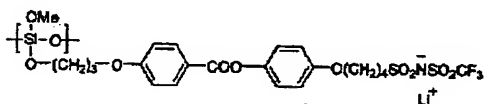
[Formula 9]



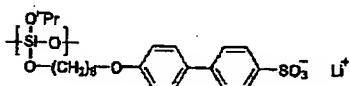
(P-17) $\text{Y} = \text{Li}^+$
 (P-18) $\text{Y} = \text{H}_3\text{C}-\text{N}^+ \text{C}_6\text{H}_4 \text{N}^+ \text{CH}_2\text{CH}_3$



(P-19) $\text{Y} = \text{Li}^+$
 (P-20) $\text{Y} = \text{H}_3\text{C}-\text{N}^+ \text{C}_6\text{H}_4 \text{N}^+ \text{CH}_2\text{CH}_3$



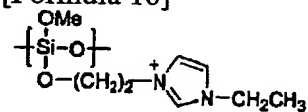
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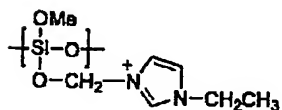
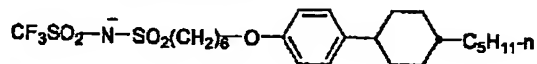
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[0050]

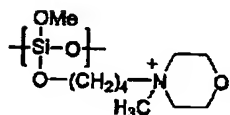
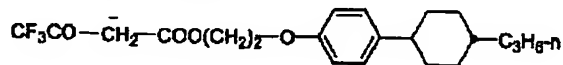
[Formula 10]



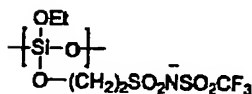
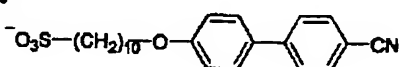
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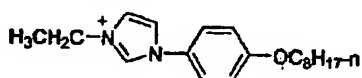
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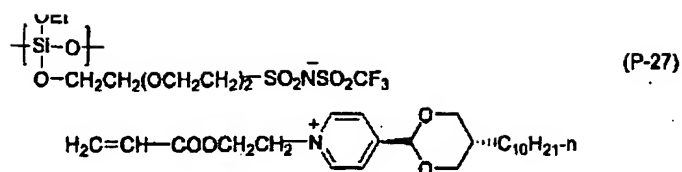


(P-25)



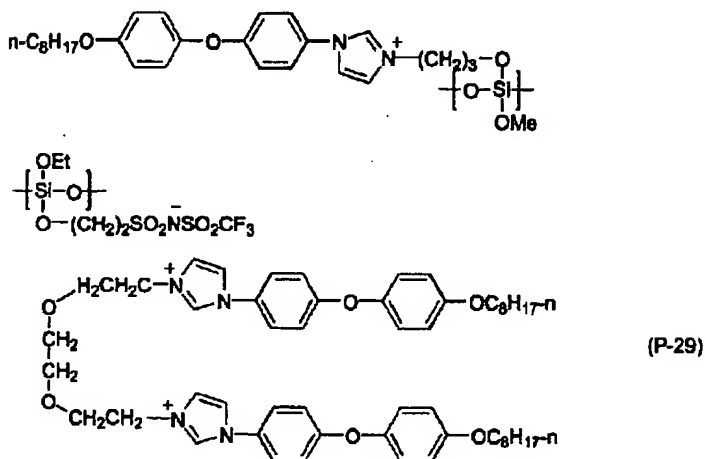
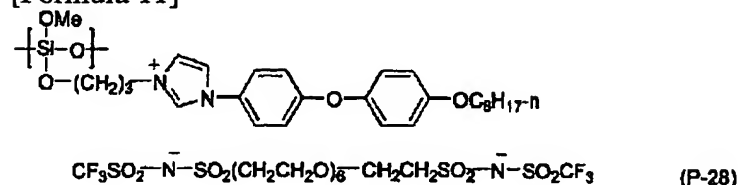
(P-26)





[0051]

[Formula 11]



[0052] A specific liquid crystal compound may be a high molecular compound obtained by having a polymerization nature machine and carrying out the polymerization of them. The radical polymerization method which is a general macromolecule synthesis method indicated by the laboratory procedure (Kagaku-Dojin) of Takayuki Otsu and Kinoshita **** collaboration: macromolecule composition, Takayuki Otsu: lecture polymerization-reaction theory 1 radical polymerization (I), and (Kagaku-Dojin) as a polymerization method which this high molecular compound obtains can be used. The thermal polymerization initiator which there are a thermal polymerization method using a thermal polymerization initiator and the photopolymerizing method using a photopolymerization initiator, and is used preferably For example, 2 and 2'-azobis (isobutyronitrile), 2, and 2'-azobis (2,4-dimethylvaleronitrile), Azo system initiators, such as a dimethyl 2 and 2'-azobis (2-methyl propionate), For the example of the photopolymerization initiator which peroxide system initiators, such as benzoyl peroxide, etc. are contained and is used preferably alpha-carbonyl compound (U.S. JP,2367661,B -- said -- each specification publication of No. 2367670) -- The acyloin ether (U.S. JP,244828,B specification publication), alpha-hydrocarbon substitution aromatic acyloin compound (U.S. JP,2722512,B specification publication), a polynuclear quinone compound (U.S. JP,3046127,B -- said -- each specification publication of No. 2951758) -- The combination of a triaryl imidazole dimer and p-aminophenyl ketone (U.S. JP,35493676,B specification publication), An acridine, a phenazine compound (JP,60-105667,A, the U.S. JP,4239850,B specification publication), and an OKISA diazole compound (U.S. JP,4212970,B specification publication) are contained. The desirable addition of a polymerization initiator is below 20 mass % more than 0.01 mass % to a monomer (salt) total amount, and is below 10 mass % more than 0.1 mass % still more preferably. The desirable molecular weight (number average molecular weight) of the macromolecule obtained by the polymerization is 5,000-1 million, when monomers

(salt) are single organic functions, and it is 10,000-500,000 still more preferably. Moreover, when the case of polyfunctional monomer (salt) or a cross linking agent is used, the polymer of the above-mentioned molecular weight forms the 3-dimensional network structure.

[0053] When using the electrolyte constituent of this invention for the electrolyte of a photoelectrochemical cell, it is desirable to use the electrolyte constituent containing I⁻ and I₃⁻ as a charge carrier, and it can add them in the form of arbitrary salts. As an opposite cation of a desirable iodine salt, the above-mentioned general formula (III-a) or (III-b) (III-c) the thing expressed is mentioned. As for an I₃⁻-salt, it is common to add iodine (I₂) to the bottom of I-salt existence, and to make it generate in an electrolyte constituent. Added I₃⁻ of I₂ and the amount of said generates in that case.

[0054] The concentration of I⁻ in the electrolyte constituent of this invention has desirable 10 - 90 mass %, and its 30 - 70 mass % is still more desirable. It is desirable that all the components of the remainder in that case are specific liquid crystal compounds. In addition, this concentration is the concentration also containing this, when I⁻ is contained as a counter ion in the aforementioned specific liquid crystal compound.

[0055] It is more desirable that it is [0.1-20 mol] %, as for I₃⁻, it is desirable that it is [0.1-50 mol / of I⁻] %, and it is / it is still more desirable that it is / 0.5-10 mol / %, and / most desirable that it is / 0.5-5 mol / %. In addition, this rate is this ***** rate, when I₃⁻ is contained as a counter ion in the aforementioned specific liquid crystal compound.

[0056] The fused salt which may also contain still more nearly another fused salt in the electrolyte constituent of this invention, and is used preferably The aforementioned general formula (III-a), and (III-b) (III-c) the shown organic cation and arbitrary anions are combined. as an anion Halogenide ion, SCN⁻ (Cl⁻, Br⁻, etc.), BF₄⁻, PF₆⁻, ClO₄⁻, 2 (CF₃SO₂)N⁻, 2 (CF₃CF₂SO₂)N⁻, CH₃SO₃⁻, CF₃SO₃⁻, CF₃COO⁻, Ph₄B⁻, 3(CF₃SO₂) C⁻, etc. are mentioned as a desirable example, and SCN⁻, CF₃SO₃⁻, CF₃COO⁻, 2 (CF₃SO₂)N⁻, and BF₄⁻ are mentioned still more preferably. Moreover, it is desirable that alkali-metal salts, such as LiI, CF₃COOLi, CF₃COONa, LiSCN, and NaSCN, are especially included from a viewpoint on the photoelectrical flow direction. As for the addition of an alkali-metal salt, it is desirable that it is a 0.02 - 2 mass % grade, and its 0.1 - 1 mass % is still more desirable.

[0057] To the electrolyte constituent of this invention, metal iodides, such as LiI, NaI, KI, CsI, and CaI₂, The iodine salt of the 4th class imidazolium compound, the iodine salt of a tetraalkylammonium compound, Metal bromides, such as Br₂, LiBr, NaBr, KBr, CsBr, and CaBr₂, Or the bromine salt of the 4th class ammonium compounds, such as Br₂, a tetrapod alkylammonium star's picture, and a pyridinium star's picture Sulfur compounds, such as metal complexes, such as a ferrocyanic-acid salt-ferricyanic-acid salt and a ferrocene-ferricinium ion, the poly sodium sulfide, and alkyl thiol-alkyl disulfide, viologen coloring matter, a hydroquinone-quinone, etc. are made to contain, and can also be used. When making it contain, as for the amount of these compounds used, it is desirable that it is below 30 mass % of the whole electrolyte constituent.

[0058] the liquid crystal compound and ** of the aforementioned specification in the electrolyte constituent of this invention -- ** -- a solvent can both be preferably used to this compound and a homogeneous amount at the maximum

[0059] As for the solvent used for the electrolyte constituent of this invention, it is desirable for a dielectric constant to be high in improving ionic mobility low, and for viscosity to be the compound which improves effective carrier concentration and can discover the outstanding ion conductivity. As such a solvent, carbonate compounds, such as ethylene carbonate and propylene carbonate, Heterocyclic compounds, such as 3-methyl-2-oxazolidinone, a dioxane, Ether compounds, such as diethylether, ethylene glycol dialkyl ether, The propylene-glycol dialkyl ether, the polyethylene-glycol dialkyl ether, Chain-like ether, such as the polypropylene-glycol dialkyl ether, A methanol, ethanol, ethylene glycol monoalkyl ether, Propylene-glycol monoalkyl ether, polyethylene-glycol monoalkyl ether, Alcohols, such as polypropylene-glycol monoalkyl ether, Ethylene glycol, a propylene glycol, a polyethylene glycol, Polyhydric alcohol, such as a polypropylene glycol and a glycerol, an acetonitrile, Guru taro dinitrile, a methoxy acetonitrile, a propionitrile, Non-proton polar substances, such as ester, such as nitril compounds, such as a benzonitrile, a carboxylate, phosphoric ester, and phosphonate, a dimethyl sulfoxide, and a sulfolane, water, etc. can be used. Also in this, nitril

compounds, such as heterocyclic compounds, such as carbonate compounds, such as ethylene carbonate and propylene carbonate, and 3-methyl-2-oxazolidinone, an acetonitrile, guru taro dinitrile, a methoxy acetonitrile, a propionitrile, and a benzonitrile, and especially ester are desirable. Even if it uses these independently, they may use two or more sorts together.

[0060] As a solvent, the boiling point [in / an ordinary pressure (one atmospheric pressure) / at the viewpoint of the improvement in endurance by volatility-proof] has desirable 200 degrees C or more, its 250 degrees C or more are more desirable, and its 270 degrees C or more are still more desirable.

[0061] in using the electrolyte constituent of this invention for electrochemical cells, such as a lithium ion battery, at least one kind of the compound in an electrolyte constituent contains a lithium element (ion) -- although it comes out and a certain compound is used suitably, as concentration of a lithium element (ion), 5 % of the weight - 100 % of the weight is desirable, and 60 % of the weight is still more desirable from 20 % of the weight

[0062] The electrolyte constituent of this invention can be used for reaction solvents, such as a chemical reaction and metal plating, a CCD (charge-coupled device) camera, various electrochemical cells (the so-called cell), an electrochemistry sensor, a photoelectrical evaporation study sensor, etc. It is more desirable for it to be preferably used for a non-water rechargeable battery (especially lithium secondary battery) and the photoelectrochemical cell using the semiconductor mentioned later, and to be used for a photoelectrochemical cell.

[0063] The electrochemical cell of this invention which used the electrolyte constituent of this invention below for the [electrochemical cell] is explained. Since the electrochemical cell of this invention contains the electrolyte constituent of the aforementioned this invention, it shows the outstanding endurance and outstanding ion conductivity.

[0064] Except the electrochemical cell of this invention containing the electrolyte constituent of the aforementioned this invention as an electrolyte, there is especially no limit and it can take general composition. A general electrochemical cell becomes by composition which sandwiched the electrolyte by the operation pole and the counter electrode, and corresponding to the oxidization (reduction) reaction which occurs by operation best quality, and the reduction (oxidization) reaction which occurs by the counter electrode, when the carrier ion in an electrolyte moves between two poles, it functions. In the case of the photoelectrochemical cell mentioned later, in the case of the electrode (for example, coloring matter sensitization semiconductor electrode) and rechargeable battery from which an operation pole produces electromotive force by optical pumping, the active material which can carry out insertion discharge of the lithium ion in connection with oxidation reduction is used by an operation pole (usually called a positive electrode) and the counter electrode (usually called a negative electrode).

[0065] The photoelectrochemical cell of this invention which used the electrolyte constituent of this invention below for the [photoelectrochemical cell] is explained. The photoelectrochemical cell of this invention has the charge transporting bed which contains an electrolyte constituent on a conductive base material, a photosensitive layer containing the semiconductor by which sensitization was carried out with coloring matter, and a counter electrode, and it constitutes them so that the optoelectric transducer explained to the so-called following may be made to work in an external circuit. The photoelectrochemical cell of this invention shows the outstanding endurance with small degradation of the cell performance in the passage of time while it is excellent in a photo-electric-translation performance, since the aforementioned charge transporting bed contains the electrolyte constituent of this invention.

[0066] [1] An example of an optoelectric transducer applicable to this invention at optoelectric-transducer drawing 1 is shown. A conductive layer 12, an under coat 14, a photosensitive layer 16, the charge transporting bed 18, and the counter electrode conductive layer 20 come to carry out the laminating of the optoelectric transducer 10 one by one. A photosensitive layer 16 turns into the semiconductor layer 24 which carried out sensitization with coloring matter d from the charge transportation material t. The semiconductor layer 24 is a porous layer which consists of a semiconductor particle s, the opening was formed between the semiconductor particles s and the charge transportation material t has permeated this opening. The charge transportation material t consists of the same component as the material used for the charge transporting bed 18. Under the

conductive layer 12, the substrate 28 is arranged on the substrate 26 and the counter electrode conductive layer 20. Substrates 26 and 28 may be for giving intensity, and may not be in an optoelectric transducer. Moreover, on the boundary of each layer, for example, the boundary of a conductive layer 12 and a photosensitive layer 16, the boundary of a photosensitive layer 16 and the charge transporting bed 18, and the boundary of the charge transporting bed 18 and the counter electrode conductive layer 20, the constituents of each class may be carrying out diffusive mixing mutually. In addition, a conductive layer 12, a substrate 26, and/or the counter electrode conductive layer 20 and substrate 28 of the side which may carry out incidence of the light to an optoelectric transducer 10 from either or both sides, and carries out incidence of the light to it can consist of material which has light-transmission nature, respectively.

[0067] Next, an operation of an optoelectric transducer 10 is explained. In addition, the case where the semiconductor particle *s* is *n* type is explained. If light carries out incidence to an optoelectric transducer 10, the light which carried out incidence will reach a photosensitive layer 16, will be absorbed with coloring matter *d* etc., and will generate the coloring matter *d* of an excitation state. The excited coloring matter *d* passes the electron of a high energy to the conduction band of the semiconductor particle *s*, and it becomes an oxidant itself. The electron from which it moved to the aforementioned conduction band reaches a conductive layer 12 by the network of the semiconductor particle *s*. Therefore, a conductive layer 12 has an electronegative potential to the counter electrode conductive layer 20. In the mode which used the optoelectric transducer 10 for the photoelectric cell, if this photoelectric cell is connected with an external circuit, the electron in a conductive layer 12 will reach the counter electrode conductive layer 20, working in an external circuit. The generated reductant (for example, I_3^-) returns the oxidant of coloring matter *d*, and returns an electron while it returns this electrolyte component (for example, I^-), when charge transportation material is an electrolyte. By continuing irradiating light, a series of reactions occur succeeding and can take out the electrical and electric equipment.

[0068] Hereafter, an usable material and its formation method are explained to each class of the aforementioned optoelectric transducer. In addition, below, when calling it "a conductive base material", it is accepted conductive-layer 12, and although it consists of a conductive layer 12 and a substrate 26 which it is arbitrary and is prepared, when calling it a "counter electrode" including both sides, it is accepted counter electrode conductive-layer 20, and both sides are included although it consists of a counter electrode conductive layer 20 and a substrate 28 which it is arbitrary and is prepared.

[0069] (A) A conductive base material conductivity base material consists of the monolayer of (1) conductive layer or (2) conductive layers, and two-layer [of a substrate]. In the case of (1), material at which intensity and sealing performance are fully maintained as a conductive layer is used, for example, a metallic material (alloys containing these, such as platinum, gold, silver, copper, zinc, titanium, and aluminum) can be used. In the case of (2), the substrate which has the conductive layer which contains an electric conduction agent in a photosensitive-layer side can be used. As a desirable electric conduction agent, a metal (for example, alloys containing these, such as platinum, gold, silver, copper, zinc, titanium, aluminum, and an indium), carbon, or conductive metallic oxides (what doped a fluorine or antimony to an indium-tin multiple oxide and the tin oxide) are mentioned. The thickness of a conductive layer has desirable about 0.02-10 micrometers.

[0070] A conductive base material has surface electrical resistance as good as a low. The ranges of desirable surface electrical resistance are below 50ohms / **, and are below 20ohms / ** still more preferably.

[0071] When irradiating light from a conductive base material side, as for a conductive base material, it is desirable that it is substantially transparent. It means substantially that permeability is it 10% or more that it is transparent in some or the whole region of light of a visible - near infrared region (400-1200nm), it is desirable that it is 50% or more, and 80% or more is more desirable. It is desirable that the permeability of the wavelength region where a photosensitive layer has sensitivity especially is high.

[0072] What formed the transparent conductive layer which consists of a conductive metallic oxide in the front face of transparent substrates, such as glass or plastics, by an application or vacuum

evaporation as a transparent conductivity base material is desirable. A thing desirable as a transparent conductive layer is the diacid-ized tin or indium-stannic-acid ghost (ITO) which doped a fluorine or antimony. A transparent polymer film besides glass substrates, such as an advantageous soda glass and an alkali free glass without the influence of alkali elution, can be used for a transparent substrate in respect of a low cost and intensity. As a material of a transparent polymer film, there is a triacetyl-cellulose (TAC), polyethylene-terephthalate (PET), polyethylenenaphthalate (PEN), syndiotactic polystyrene (SPS), polyphenylene-sulfide (PPS), polycarbonate (PC), polyarylate (PAr), polysulfone (PSF), polyester sulfone (PES), polyimide (PI), polyether imide (PEI), annular polyolefine, and bromine-ized phenoxy etc. In order to secure sufficient transparency, as for the coverage of a conductive metallic oxide, it is desirable to consider as per [0.01-100g] two 1m of base materials of glass or plastics.

[0073] It is desirable to use a metal lead in order to lower resistance of a transparent conductivity base material. The quality of the material of a metal lead has desirable metals, such as platinum, gold, nickel, titanium, aluminum, copper, and silver. As for a metal lead, it is desirable to install in a transparent substrate by vacuum evaporation, sputtering, etc., and to prepare on it the transparent conductive layer which consists of the conductive tin oxide or a conductive ITO film. The fall of the amount of incident lights by metal lead installation may be 1 - 5% more preferably less than 10%.

[0074] (B) The photosensitive-layer aforementioned photosensitive layer absorbs light, performs charge separation, and has the function which produces an electron and an electron hole. The aforementioned photosensitive layer contains the semiconductor by which coloring matter sensitization was carried out. With the semiconductor by which coloring matter sensitization was carried out, generating of an optical absorption, the electron by this, and an electron hole takes place mainly in coloring matter, and a semiconductor bears the role which receives and transmits this electron (or electron hole). As for the semiconductor used by this invention, it is desirable that it is the n-type semiconductor which gives an anode current by a conductor electron serving as a carrier under optical pumping.

[0075] (1) The compounds (for example, a strontium titanate, titanate-acid calcium, titanate-acid sodium, a barium titanate, a niobic-acid potassium, etc.) which have silicon, an element semiconductor like germanium, a III-V system compound semiconductor, metal chalcogenide (for example, an oxide, a sulfide, selenides, or those composites etc.), or a perovskite structure as a semiconductor semiconductor can be used.

[0076] As chalcogenide of a desirable metal, the oxide of titanium, tin, zinc, iron, a tungsten, a zirconium, a hafnium, strontium, an indium, a cerium, an yttrium, a lanthanum, vanadium, niobium, or a tantalum, cadmium, zinc, lead, silver, antimony or the sulfide of a bismuth, cadmium or a leaden selenide, the telluride of cadmium, etc. are mentioned. As other compound semiconductors, the selenide of phosphides, such as zinc, a gallium, an indium, and cadmium, a gallium arsenide, or a copper-indium, the sulfide of a copper-indium, etc. are mentioned. Furthermore, the composite expressed with $MxOySz$ or $M1xM2yOz$ (the number [metallic element] of combination with which an oxygen atom, x, and y and z become as for M, M1, and M2, and, as for O, a valence becomes neutral, respectively) can also be used preferably.

[0077] The desirable example of the semiconductor used for this invention Si, TiO_2 , SnO_2 , Fe_2O_3 , WO_3 , ZnO , Nb_2O_5 , CdS , ZnS and PbS , Bi_2S_3 , $CdSe$, $CdTe$, They are $SrTiO_3$, GaP , InP , $GaAs$, $CuInS_2$, and $CuInSe_2$ grade. More preferably TiO_2 , ZnO , SnO_2 , Fe_2O_3 , WO_3 , Nb_2O_5 , CdS , It is PbS , $CdSe$, $SrTiO_3$ and InP , $GaAs$, and $CuInS_2$ and $CuInSe_2$, is TiO_2 and Nb_2O_5 especially preferably, and is TiO_2 most preferably. TiO_2 which includes an anatase type crystal 70% or more is desirable especially desirable, and TiO_2 is TiO_2 of 100% anatase type crystal. Moreover, it is the purpose which raises the electronic conductivity in these semiconductors, and it is also effective to dope a metal. As a metal to dope, divalent and a trivalent metal are desirable. It is the purpose which prevents that a reverse current flows from a semiconductor to a charge transporting bed, and it is also effective to dope a univalent metal to a semiconductor.

[0078] Although a single crystal or a polycrystal is sufficient as the semiconductor used for this invention, from viewpoints, such as a manufacturing cost, raw-material reservation, and an energy pay back time, a polycrystal is desirable and especially the porous membrane that consists of a

semiconductor particle is desirable. Moreover, the amorphous portion may be included in part.

[0079] Although the particle size of a semiconductor particle is generally the order of nm- μ m, as for the mean particle diameter of the primary particle which asked for projected area from the diameter when converting into a circle, it is desirable that it is 5-200nm, and its 8-100nm is more desirable. Moreover, the mean particle diameter of the semiconductor particle in dispersion liquid (aggregated particle) has desirable 0.01-30 micrometers. It is 10nm or less preferably [may mix two or more kinds of particles from which a particle size distribution differs, and / that the average size of a small particle is 25nm or less in this case], and more preferably. Particle size is big, for example, it is also desirable to mix a semiconductor particle (100nm or more and about 300nm) in order to scatter an incident light and to raise the rate of optical capture.

[0080] You may be two or more sorts of mixtures from which the kind of semiconductor particle also differs. When mixing and using two or more sorts of semiconductor particles, as for one sort, it is desirable that they are TiO₂, ZnO, Nb₂O₅, or SrTiO₃. Moreover, it is desirable that they are SnO₂, Fe₂O₃, or WO₃ as one more sort. As a still more desirable combination, combination, such as ZnO, SnO₂, ZnO and WO₃, or ZnO, SnO₂, WO₃, can be mentioned. When mixing and using two or more sorts of semiconductor particles, each particle size may differ. The particle size of the semiconductor particle mentioned especially at the one above-mentioned item is large, and combination with the small semiconductor particle mentioned henceforth [2 items] is desirable. The particle of a desirable large particle size is 100nm or more, and the particle of a small particle size is 15nm or less in combination.

[0081] As a method of producing a semiconductor particle, they are the company (1998) of the "science of sol-gel method" AGUNE ** style of *****, and a technical-information association.

[Translation done.]

* NOTICES *

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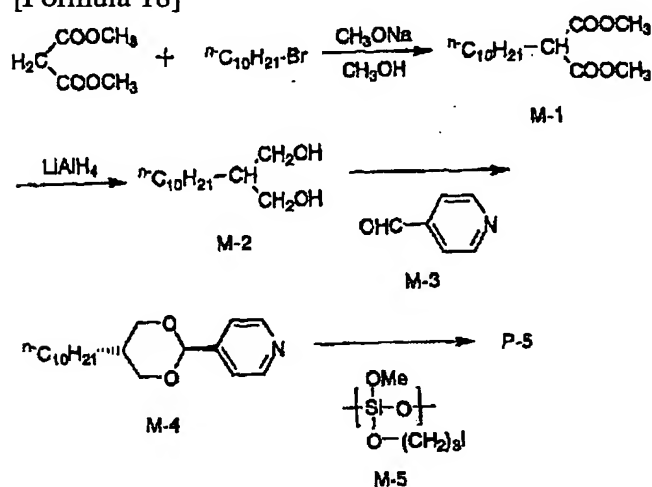
EXAMPLE

[Example] Hereafter, an example explains this invention concretely.

- The instantiation compound P-5 was compounded by the synthetic example-following composition scheme of the instantiation compound P-5.

[0156]

[Formula 18]



[0157] ** The synthetic dimethyl malonate of intermediate field M-1; after dissolving 58.1g (439mmol) in the methanol, adding methanol 28% solution; 88ml of a sodium methoxide and dropping 1-BUROMO decane 97.2g (439mmol) over 1 hour, it flowed back for 8 hours. Diluted hydrochloric acid was filled with reaction mixture, and ethyl acetate extracted after neutralization. Vacuum concentration of the extraction solution was carried out after dryness with magnesium sulfate, vacuum distillation of the residue was carried out, and M-1 [41g (fraction (399Pa (3mmHg) / 82 degrees C))] was obtained.

[0158] ** The solution which was obtained by the above-mentioned ** and which dissolved M-1 (41g, 170mmol) in diethylether (50ml) was dropped over 2 hours, having distributed the synthetic lithium aluminum hydride (11g, 289mmol) of intermediate field M-2 to 150ml diethylether, and stirring at a room temperature. After dropping, after flowing back for 3 hours, diluted hydrochloric acid/ice was slowly filled with reaction mixture, and it extracted, after making a solution acid. The bottom solvent of reduced pressure was distilled off for the extract after dryness with magnesium sulfate, and the oily matter of 31g of rough products was obtained. The rough product was refined in silica gel column chromatography, and 14g was obtained as M-2 and colorless oily matter.

[0159] ** M-2 (13.85g, 64mmol) obtained by the synthetic above of intermediate field M-4 and M-3 (6.86g, 64mmol) were distributed in toluene (50ml), Para toluenesulfonic acid (12g) was added, and heating reflux was carried out for 5 hours, distilling off water. The water (100ml) which added potassium carbonate (10g) was filled with reaction mixture, ethyl acetate extracted, and the solvent was distilled off under reduced pressure after drying an extract. The residue was recrystallized in the acetonitrile, and M-4 of the purpose was considered as the crystal, and was obtained 7g.

[0160] ** It distributed to the acetonitrile (50ml) and the dimethylacetamide (20ml), and M-4 (5g, 16.4mmol) and polymer M-5 (3g) which were obtained by the synthetic above of P-5 were made to

react at 80 degrees C for 10 hours. The solvent was distilled out of reaction mixture at 120 degrees C under reduced pressure, and P-5 (7.5g) which has the mesomorphism side chain which is the specified substance was obtained.

[0161] (Example 1)

- With 15g [of titanium dioxides] (Japanese Aerosil Degussa P-25), 45g, 1g (Aldrich make, Triton X-100), and a diameter of 0.5mm zirconia-beads (Nikkato Corp. make) 30g was put into the vessel made from stainless steel of 200ml of content volume which carried out Teflon (registered trademark) coating of the manufacture inside of photoelectrochemical-cell-1-1. titanium-dioxide dispersion liquid, and it distributed in 1500rpm for 2 hours using the Sand-grinder mill (product made from eye MEKKUSU) Zirconia beads were filtered and removed from the distributed object. The mean particle diameter of the titanium dioxide in this case was 2.5 micrometers. The particle size at this time is measured in the master sizer made from MALVERN.

[0162] 1-2. The glass rod was used and the above-mentioned dispersion liquid were applied to the electric conduction side side of the electrically conductive glass (what carried out cutting processing of the Asahi Glass TCO glass-U at the 20mmx20mm size) which coated the tin oxide which doped the production fluorine of TiO₂ electrode (electrode A) which adsorbed coloring matter. Under the present circumstances, the adhesive tape was stretched to the part by the side of an electric conduction side (from an edge to 3mm), and it considered as the spacer, and glass was put in order and it applied eight sheets at a time at once so that an adhesive tape might come to ends. After the application, it exfoliated and the adhesive tape was air-dried for one day at the room temperature. Next, this glass was put into the electric furnace (muffle furnace FP-32 type made from the Yamato science), and it calcinated for 30 minutes at 450 degrees C. It flooded with the ethanol solution (3xten - four mols/(l.)) of coloring matter R-1 for 3 hours, after taking out this glass and cooling. After being immersed in a 4-tert-butyl pyridine for 15 minutes, the air drying of the glass which coloring matter dyed was washed and carried out by ethanol. Thus, the thickness of the photosensitive layer obtained is 10 micrometers, and the coverage of a semiconductor particle was taken as 20 g/m². In addition, the surface electrical resistance of electrically conductive glass was about 30ohm/**.

[0163] 1-3. The acetonitrile was distilled off, applying the acetonitrile solution (an acetonitrile being a constituent and a homogeneous amount) of the electrolyte constituent (E-102 to E-113) containing Table 1 therefore the adjusted aforementioned specific liquid crystal compound, or a comparison compound to the TiO₂ electrode substrate (1cmx1cm) which is the production **** of a photoelectrochemical cell, and was made and produced and by which the color sensitizing was carried out, and infiltrating it into TiO₂ electrode under 60 degrees C and reduced pressure. The platinum vacuum evaporationo glass of the same size was laid on top of these electrodes, and the photoelectrochemical cell (sample B-102-113) was obtained. Moreover, after laying the electrolytic solution (E-101 of Table 1) using the solvent on top of the same TiO₂ electrode substrate (2cmx2cm) as the above by which coloring matter sensitization was carried out with the platinum vacuum evaporationo glass of the same size as the electrode, it infiltrated the electrolytic solution into the crevice between both glass using capillarity, and produced the photoelectrochemical cell (sample B-101).

[0164] The photoelectrochemical cell by which the laminating of the platinum layer 6 and glass 7 which serve as electrically conductive glass 1 (that by which the conductive layer 3 was ****(ed) on glass 2), a photosensitive layer 4 (TiO two-layer coloring matter was made to stick to), the electrolyte layer 5, and a counter electrode by this example as shown in drawing 2 was carried out to order was produced.

[0165]

[Table 1]

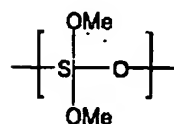
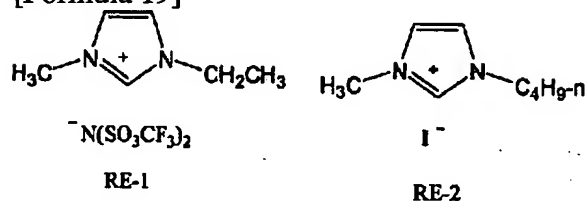
表1 電解質の組成

電解質	組成 (質量%)	サンプル	備考
E-101	(C ₄ H ₉) ₄ N ⁺ I ⁻ (48)/BCE(50)/I ₂ (2)	B-101	比較
E-102	(C ₄ H ₉) ₄ N ⁺ I ⁻ (48)/RE-1(50)/I ₂ (2)	B-102	比較
E-103	RE-2(48)/RE-1(50)/I ₂ (2)	B-103	比較
E-104	(C ₄ H ₉) ₄ N ⁺ I ⁻ (48)/RE-3(50)/I ₂ (2)	B-104	比較
E-105	P-5 (98) /I ₂ (2)	B-105	本発明
E-106	P-8 (98) /I ₂ (2)	B-106	本発明
E-107	P-11 (98) /I ₂ (2)	B-107	本発明
E-108	P-14 (98) /I ₂ (2)	B-108	本発明
E-109	P-5 (48) /P-6(50)/I ₂ (2)	B-109	本発明
E-110	P-8 (48) /P-9(50)/I ₂ (2)	B-110	本発明
E-111	P-8 (48) /P-10(50)/I ₂ (2)	B-111	本発明
E-112	P-11 (48) /P-12(50)/I ₂ (2)	B-112	本発明
E-113	P-11 (48) /P-13(50)/I ₂ (2)	B-113	本発明

BCE (溶媒) : ビスシアノエチルエーテル

[0166]

[Formula 19]



[0167] 1-4. By letting AM1.5 filter (product made from Oriel), and a sharp cut filter (KenkoL-41) pass for the light of the xenon lamp of measurement 500W of a photoelectric conversion efficiency (USHIO make), the simulation sunlight which does not include ultraviolet rays was generated and this luminous intensity was adjusted to 100 mW/cm².

[0168] The electrical and electric equipment which connected the crocodile clip, respectively, irradiated simulation sunlight at 70 degrees C, and was generated on the above-mentioned electrically conductive glass and above-mentioned platinum vacuum evaporation glass of a photoelectrochemical cell was measured in the current-potential measuring device (case rhe SMU238 type). the open circuit voltage (Voc) of the photoelectrochemical cell called for by this, short-circuit current density (Jsc), and a form factor -- (FF) [= maximum output/(open-circuit-voltage x short-circuit current)] and a conversion efficiency (eta), and constant temperature -- the decreasing rate of the short-circuit current density after carrying out the passage of time for 400 hours was collectively indicated to Table 2 under constant humidity (60 degrees C, 70%R.H.)

[0169]

[Table 2]

表2 光電変換性能

サンプル	J _{sc} (mA/m ²)	V _{oc} (V)	FF	η (%)	J _{sc} 低下率(%) 80℃-湿度70% 400時間	備考
B-101	11.3	0.60	0.65	4.4	99	比較
B-102	8.1	0.56	0.54	2.4	45	比較
B-103	8.5	0.54	0.56	2.6	23	比較
B-104	8.9	0.57	0.57	3.0	10	比較
B-105	10.4	0.66	0.67	4.5	3	本発明
B-106	10.3	0.66	0.68	4.3	4	本発明
B-107	10.5	0.67	0.66	4.6	3	本発明
B-108	10.6	0.67	0.65	4.6	5	本発明
B-109	11	0.62	0.64	4.3	6	本発明
B-110	11	0.63	0.65	4.5	6	本発明
B-111	11	0.63	0.63	4.4	5	本発明

試料名	電極面積 (cm ²)	短絡電流密度 (mA/cm ²)	開放電圧 (V)	形状因子	変換効率 (%)	備考
B-112	10.7	0.65	0.64	4.5	5	本発明
B-113	10.5	0.65	0.64	4.3	4	本発明

Jsc : 短絡電流密度、Voc : 開放電圧、FF : 形状因子、 η : 変換効率

[0170] From the above-mentioned result, since a solvent volatilizes, the photoelectrochemical cell (B-101) using the solvent as the electrolytic solution is understood that endurance is very bad. Moreover, by passing, although the cell (B-104) using polysiloxane RE-3 which do not have fused salt RE-1, the cell (B-102, B-103) using RE-2, and mesomorphism substituent of a comparison compound is small, it understands that a photo-electric-translation performance is not enough for degradation in the time. The photoelectrochemical cell using the electrolyte constituent containing the aforementioned specific liquid crystal compound is excellent in initial performances, such as short-circuit current density and a conversion efficiency, and endurance to them. Such an effect was seen when which coloring matter was used.

[0171] (Example 2)

- As a Production Positive Active Material of Lithium Rechargeable Battery-2-1. Positive-Electrode Sheet LiCoO₂ 43 weight sections, the scale-like graphite 2 weight section, the acetylene black 2 weight section, Furthermore, add the polyacrylonitrile 3 weight section as a binder, and the slurry which kneaded the acrylonitrile 100 weight section as a medium, and was obtained is painted on an aluminum foil with a thickness of 20 micrometers using an extrusion formula application machine. After pressing with the calender press machine after dryness, the lead board made from aluminum was welded to the edge, and the positive-electrode sheet with 95 micrometers [in thickness] and a width-of-face [of 54mm] x length of 49mm was produced.

[0172] 2-2. as the production negative-electrode active material of a negative-electrode sheet -- a meso face pitch system carbon material (PETOKA) -- as 43 weight sections and an electric conduction agent -- the acetylene black 2 weight section and the graphite 2 weight section -- comparatively -- coming out -- mixing -- further -- as a binder -- a polyacrylonitrile -- 3 weight sections -- adding -- the N-methyl pyrrolidone 100 weight section -- as a medium -- kneading -- a negative electrode -- a mixture -- the slurry was obtained a negative electrode -- a mixture -- the slurry was painted on copper foil with a thickness of 10 micrometers using the extrusion formula application machine, it pressed with the calender press machine after dryness, and the negative-electrode sheet with 46 micrometers [in thickness] and a width-of-face [of 55mm] x length of 50mm was produced After welding the lead board made from nickel to the edge of a negative-electrode sheet, it heat-treated at 230 degrees C for 1 hour in dry air of -40 degrees C or less of dew-points. Heat treatment was performed using the far-infrared heater.

[0173] The production negative-electrode sheet of a 2-3. sheet cell and the positive-electrode sheet carried out dehydration dryness at 230 degrees C for 30 minutes in dry air of -40 degrees C or less of dew-points, respectively. In dry atmosphere, the laminating of the separator (polyethylene porosity film) and nonwoven fabric which were judged in a dried [dehydration] positive-electrode sheet with a width-of-face [of 54mm] x length of 49mm and width-of-face [of 60mm] x length of 60mm was carried out, the liquid which dissolved the electrolyte (E-202-213) of composition adjusted according to Table 3 on the nonwoven fabric in the acetonitrile of the amount of said was applied, and the acetonitrile was distilled off under reduced pressure at 50 degrees C. Moreover, the electrolytic solution (E-201) using the solvent was infiltrated into the nonwoven fabric as it is. The laminating of the dried [dehydration] negative-electrode sheet with a width-of-face [of 55mm] x length of 50mm was carried out on it, using the sheathing material which consists of a laminate film of a polyethylene (50 micrometers)-polyethylene terephthalate (50 micrometers), heat weld was carried out, four edges were sealed under the vacuum, and the sheet type cell (sample B-201-213) was produced.

[0174] The sheet type cell by which the laminating of the positive-electrode sheet 31 equipped with the negative-electrode sheet 33 equipped with the negative-electrode terminal 35, the solid polymer electrolyte 32, and the positive-electrode terminal 34 by this example as shown in drawing 3 was carried out to order was produced.

[0175]

[Table 3]

表3 電解質の組成

電解質番号	電解質組成 (質量%)	電池番号	備考
E-201	RE-4(30)/PC(30)/EC(40)	B-201	比較
E-202	RE-4(30)/RE-1(70)	B-202	比較
E-203	RE-4(30)/PG1000	B-203	比較
E-204	LiClO ₄ (30)/RE-3(70)	B-204	比較
E-205	P-17(100)	B-205	本発明
E-206	P-19(100)	B-206	本発明
E-207	P-21(100)	B-207	本発明
E-208	P-22(100)	B-208	本発明
E-209	P-17(50)/P-18(50)	B-209	本発明
E-210	P-19(50)/P-20(50)	B-210	本発明
E-211	RE-3(30)/P-18(70)	B-211	本発明
E-212	RE-3(30)/P-20(70)	B-212	本発明
E-213	LiBF ₄ (30)/P-23(70)	B-213	本発明

RE-4 : LiN(SO₂CF₃)₂

PC : プロピレンカーボネート

EC : エチレンカーボネート

PG1000 : ポリエチレングリコール (平均分子量1000)

[0176] 2-4. About the sheet type cell produced by the method of the evaluation above of a cell performance, charge and discharge were repeated 30 times on condition that current density 1.3 mA/cm², charge final-voltage 4.2V, and discharge-final-voltage 2.6V**, and the service capacity in 30 cycle eye was calculated. This was investigated about five cells of the same prescription, and the average was made into the capacity of the cell. Thus, the capacity of each cell was calculated and the relative capacitor to a sample B-201 was calculated. Moreover, the service capacity of the 200 cycle eye of each cell was calculated, the ratio to the service capacity of 10 cycle eye was calculated, and it expressed as a cycle capacity. Each value was shown in Table 4.

[0177]

[Table 4]

表4 電池性能

電池番号	相対容量	サイクル容量	備考
B-201	1	0.30	比較
B-202	0.59	0.91	比較
B-203	0.31	0.77	比較
B-204	0.70	0.91	比較
B-205	0.88	0.95	本発明
B-206	0.87	0.95	本発明
B-207	0.85	0.96	本発明
B-208	0.86	0.98	本発明
B-209	0.95	0.95	本発明
B-210	0.94	0.94	本発明
B-211	0.96	0.94	本発明
B-212	0.98	0.93	本発明
B-213	0.96	0.94	本発明

[0178] It turns out that the electrolyte which contains the aforementioned specific liquid crystal compound from the above-mentioned result is raising cycle nature, without seeing the big fall of capacity.

[0179] From these examples, the electrolyte which did not volatilize substantially and was excellent in using the aforementioned specific liquid crystal compound at charge transportability ability was obtained, thereby, it excelled in the photoelectric transfer characteristic and the photoelectrochemical cell with little property degradation by the passage of time was obtained. Furthermore, this electrolyte does not reduce cell capacity and it turns out that it is the lithium ion conduction material which was moreover excellent in the cycle property.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the outline block diagram showing an example of the optoelectric transducer of this invention.

[Drawing 2] It is the cross section showing the composition of the photoelectrochemical cell produced in the example 2.

[Drawing 3] It is the schematic diagram of the sheet type cell produced in the example 3.

[Description of Notations]

1 Electrically Conductive Glass

2 Glass

3 Conductive Layer

4 Photosensitive Layer (TiO Two-layer Which Carried Out Coloring Matter Adsorption)

5 Electrolyte Layer

6 Platinum Layer

7 Glass

10 Optoelectric Transducer

12 Conductive Layer

14 Under Coat

16 Photosensitive Layer

18 Charge Transporting Bed

20 Counter Electrode Conductive Layer

24 Semiconductor Layer

26 Substrate

28 Substrate

s Semiconductor particle

d Coloring matter

t Charge transportation material

31 Positive-Electrode Sheet

32 Solid Polymer Electrolyte

33 Negative-Electrode Sheet

34 Positive-Electrode Terminal

35 Negative-Electrode Terminal

[Translation done.]

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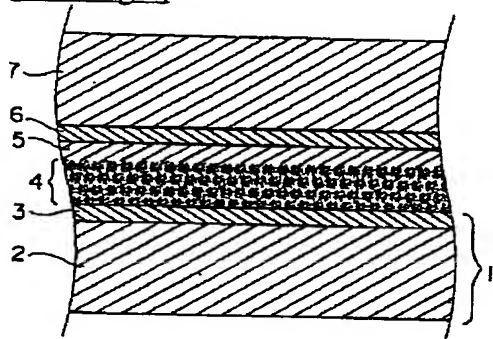
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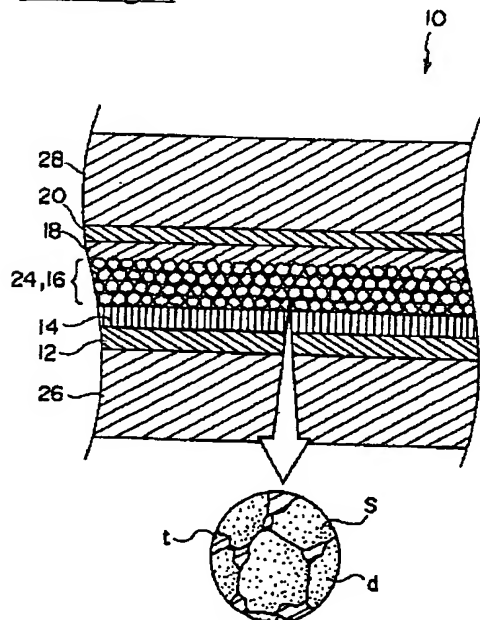
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DRAWINGS

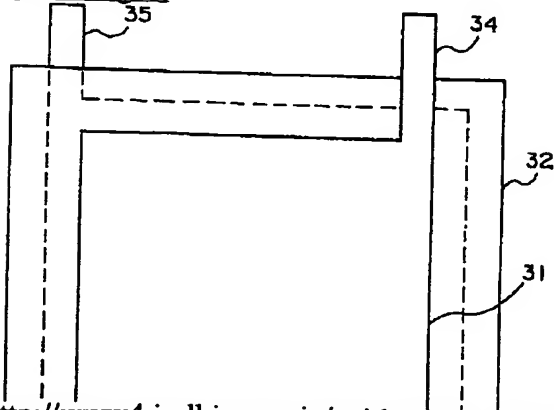
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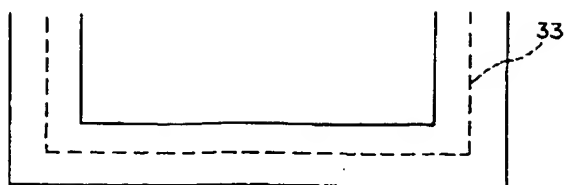


[Drawing 1]



[Drawing 3]





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